

Alternatives for Sodium Cyanide for
Flotation Control

Battelle Columbus Labs., OH

Prepared for

Industrial Environmental Research Lab.
Cincinnati, OH

Aug 81



U.S. Department of Commerce
National Technical Information Service

NTIS.

TECHNICAL REPORT DATA (Please read Instructions on the reverse before completing)		
1. REPORT NO. EPA-600/2-81-157	2. ORD Report	3. RE(P881-247439
4. TITLE AND SUBTITLE Alternatives for Sodium Cyanide for Flotation Control		5. REPORT DATE August 1981
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) E. J. Mezey, D. W. Neuendorf, G. Ray Smithson, Jr. and James F. Shea (Consultant)		8. PERFORMING ORGANIZATION REPORT NO. G-6617-0800
9. PERFORMING ORGANIZATION NAME AND ADDRESS Battelle Columbus Laboratories 505 King Ave Columbus, Ohio 43201		10. PROGRAM ELEMENT NO. 1BB610
		11. CONTRACT/GRANT NO. 68-03-2552
12. SPONSORING AGENCY NAME AND ADDRESS Indusrtial Environmental Research Laboratory Office of Research and Development U.S. Environmental Protection Agency Cincinnati, Ohio 45268		13. TYPE OF REPORT AND PERIOD COVERED Final 2/78 - 1/81
		14. SPONSORING AGENCY CODE EPA-600/12
15. SUPPLEMENTARY NOTES		
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17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Cyanide Flotation Minerals beneficiation Waste treatment Process modification Mining and milling wastes Flotation depressants		13B
REPRODUCED BY NATIONAL TECHNICAL INFORMATION SERVICE U.S. DEPARTMENT OF COMMERCE SPRINGFIELD, VA. 22161		
18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS (This Report) UNCLASSIFIED	21. NO. OF PAGES
	20. SECURITY CLASS (This page) UNCLASSIFIED	22. PRICE

ALTERNATIVES FOR SODIUM CYANIDE
FOR FLOTATION CONTROL

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory-Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This is one of a series of studies by the EPA undertaken to define data requirements and the research deemed essential to find an acceptable resolution of the problem of cyanide pollution of water released from mineral flotation processes. One approach considered here was to substitute a less toxic or nontoxic substance for cyanide rather than find a treatment process capable of removing the low concentrations of cyanide found in typical large-volume discharges from froth flotation mineral beneficiation facilities.

This study was made to determine the technical, and if possible, the economic, feasibility of substituting alternate reagents for cyanides as depressants for iron in the flotation of copper, lead, and zinc ores. The study was carried out in two phases. The first consisted of a literature search, an evaluation of the data obtained in the search, selection of the three most promising reagents indicated by the evaluation, and finally a suite of laboratory-scale flotation experiments to test the three selected reagents. These experiments were made on copper ores, copper-lead-zinc ores, and zinc ores supplied by industry. The three reagents selected and tested were sodium sulfite, sodium sulfide, and sodium thiosulfate. When the laboratory experiments indicated that these reagents did exhibit depressant potential for pyrite flotation, possibly equal to that of cyanide (also tested in parallel experiments), Phase II was undertaken. In the Phase II program, a stated initial objective was to determine the technical and economic feasibility of changing from sodium cyanide to any of the alternative reagents as pyrite depressants. The economic situation was found to be so complex that no reliable conclusions could be made under the scope of this effort.

If additional information is requested, please contact the Nonferrous Metals and Minerals Branch of the Energy Pollution Control Division.

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ABSTRACT

This was one of a series of studies by the EPA undertaken to define data requirements and the research deemed essential to find an acceptable resolution of the problem of cyanide pollution of water released from mineral flotation processes. One approach considered here was to substitute a less toxic or nontoxic substance for cyanide rather than find a treatment process capable of removing the low concentrations of cyanide found in typical large-volume discharges from froth flotation mineral beneficiation facilities.

This study was made to determine the technical, and if possible, the economic feasibility of substituting alternate reagents for cyanides as depressants for iron in the flotation of copper, lead, and zinc ores. The study was carried out in two phases. The first consisted of a literature search, an evaluation of the data obtained in the search, selection of the three most promising reagents indicated by the evaluation, and finally a suite of laboratory-scale flotation experiments to test the three selected reagents. These experiments were made on copper ores, copper-lead-zinc ores, and zinc ores supplied by industry. The three reagents selected and tested were sodium sulfite, sodium sulfide, and sodium thiosulfate.

When the laboratory experiments indicated that these reagents did exhibit depressant potential for pyrite flotation, possibly equal to that of cyanide (also tested in parallel experiments), Phase II was undertaken. In the Phase II program, a stated initial objective was to determine the technical and economic feasibility of changing from sodium cyanide to any of the alternative reagents as pyrite depressants. It was hoped that this objective might be realized by interviewing company officials and operators in the copper-lead-zinc industry. Accordingly, visits were made to 11 companies operating 17 mills in these fields. The officials of four additional mills were interviewed by phone. It became evident early in the course of this phase that the objective of determining the technical and economic feasibility of using alternative reagents for cyanide could not be achieved by this procedure. The data obtained on the mission served chiefly to show that the industry was aware of the potential for changeover, had in some cases done some work to investigate the possibility, was by and large skeptical about both the need for and the feasibility of a changeover, and could provide very little information on the technology and economics that might be involved.

Phase II was then altered to being a fact-finding mission. Phase II culminated in a plan--a reappraisal to the problem. It is believed that if the recommendations arrived at in the Phase II program are followed out, the initially desired objectives of Phase II can be achieved. The question, "Is it feasible to make the changeover and, if so, what will be the cost?", can then be definitively answered.

INTRODUCTION

Cyanide has long been looked upon as the classical poison and has been listed by EPA as a priority pollutant. The mineral dressing industry has long used cyanide in its concentration and extractive metallurgy operations. Cyanide plays a role of varying importance in the metallurgy of gold, silver, copper, nickel, cobalt, lead, zinc, molybdenum, and cadmium. In the copper, lead, and zinc industries the primary uses for cyanides are as depressants for the flotation of iron and zinc minerals and for the reactivation of copper minerals in the flotation of molybdenite.

If environmentally acceptable replacement reagents could be found that were as effective as cyanide in depressing iron, then the very worthwhile objective of eliminating a known toxic material from the environment might be realized. To this end the EPA engaged Battelle's Columbus Laboratories to investigate such a possibility.

CONCLUSIONS

The Phase I work consisted of a literature review and limited laboratory work. This research indicated that at least three reagents of relatively low toxicity might serve as alternatives for cyanide in the depression of iron flotation.

The results from these preliminary screening experiments suggest that sodium sulfide, Na_2S , and sodium sulfite, Na_2SO_3 , could approach the effectiveness of sodium cyanide, NaCN , as a pyrite depressant under the constraints of this experimental program and the ores studied. The results suggest that their use should be evaluated as an alternative to the treatment of large volumes of mining wastewater containing low concentrations of cyanide. The breadth of applicability of such alternative depressants remains unknown and must be determined. The benefits of reduced environmental effects must be weighed against possible effects on processing the continually leaner sulfide ore bodies adaptable to beneficiation by froth flotation. Losses of metal value to tailings or the misplacement of metal values into the beneficiated ore due to less selective flotation separations also may produce undesirable environmental and economic effects. Therefore, any displacement of optimized beneficiation processes based on the use of sodium cyanide as a depressant by one using an alternative pyrite depressant can have a substantial impact on an important sector of the mining industry.

A further campaign, as Phase II of the Program by Battelle in pursuit of the overall objective, revealed that a final evaluation of the project could not be made without considerable additional research and development. Most, if not all, of the companies interviewed were fully aware that alternate reagents for cyanide as depressants for iron sulfide minerals had been proposed long ago. Some had done developmental work on them. None reported favorable results.

Battelle therefore suggests a new approach, because the cyanide problem in the copper-lead-zinc industry may not be a true problem. The best and

shortest way to find out whether cyanide is a true problem is to look at the data (in the form of self-monitoring reports, compliance monitoring reports, and the reports of various biologists) in every state where copper, lead, and zinc plants or mills operate.

After reviewing these data, determine which mills are exceeding their cyanide discharge limitations, which mills are causing environmental problems, and/or which mills show no promise of correcting such conditions.

Give three options to the mills discovered through the data review: (a) close their circuits and close discharges to waters of the state; (b) apply end-of-pipe treatment to destroy cyanide in their effluent; or (c) supplant cyanide as a reagent in their process. If they accede to alternative (c) above, back them up with whatever financial support that may be available to them, to conduct laboratory research and pilot-plant work.

CONTENTS

FOREWORD	11
ABSTRACT	111
INTRODUCTION	iv
CONCLUSIONS	iv
PHASE I ALTERNATIVES FOR SODIUM CYANIDE FOR FLOTATION CONTROL	1
TASK 1. LITERATURE SEARCH	2
TASK 2. ASSESSMENT OF ALTERNATIVES TO CYANIDE AS FLOTATION CONTROL REAGENT	3
TASK 3. LABORATORY STUDIES	9
CONCLUSIONS	18
PHASE II	20
METHOD OF INVESTIGATION	20
ITEMS OBTAINED ON THE VISITS	21
SUMMARY OF RESULTS FROM THE SURVEY	22
DISCUSSION OF COST OF CONVERTING TO AN ALTERNATIVE REAGENT FOR DEPRESSING PYRITE	23
CONCLUSIONS	25
RECOMMENDATIONS	26
APPENDICES	
A. Relevant References Identified by Computer Search and Books and Articles Examined in the Literature Search	A-1
B. Basic Information Evaluation and Ranking of Depressants Uncovered in the Literature Search	B-1
C. Table C-1. Mills Visited During Study	C-1
Table C-2. Form Used for Discussion with Plant Contact	C-2
D. Data Sheets from Mills A through Q and Discussion of Data Obtained	D-1
E. Flowsheets of Typical Milling Operations	D-1

TABLES

<u>Number</u>		<u>Page</u>
1	Evaluation and Ranking Criteria for Pyrite Depressants	4
2	Pyrite Depressant Evaluation and Ranking	5
3	Dry Sieve Analysis of As-Received Ores	11
4	Wet Sieve Analysis of Ball-Milled Ores	12
5	Experimental Conditions for Batch Flotation Experiments	14
6	Chalcopyrite Ore Results	16
7	Copper-Lead-Zinc Ore Results	17
8	Zinc Ore Results	19

PHASE I

ALTERNATIVES FOR SODIUM CYANIDE FOR FLOTATION CONTROL

The economic recovery of copper, lead, and zinc from the sulfide ores of these metals in the United States always requires an initial concentration step, or steps. The flotation process is almost always a part of concentrating operations, often the major part. Flotation is a process for physically separating and collecting valuable minerals from other minerals that may be present in an ore. The process works like this: An ore is crushed and ground to such a fineness that its mineral components are "liberated"--that is, disconnected from each other and so behave characteristically in subsequent operations. The ground ore, slurried in water, is treated with various chemicals called "reagents" which have the property of attaching themselves to the surfaces of specific minerals in the mixture. The nature of the reagents is such that the coating they provide is water repellant and has an affinity for air. Fine air bubbles are then introduced into the slurry of ore in water. As they rise to the surface they come into contact with the selectively coated particles. These attach themselves to the air bubbles and are levitated to the surface of the flotation vessel, much as heavier-than-air objects can be lifted by a balloon. On the surface of the vessel the air bubbles and their burden of coated minerals collect in a "froth" which is made stable, or persistent by the use of other chemicals called "frothing agents". This froth is then scraped off the surface of the vessel or "cell" into troughs and is collected as a "concentrate" of the mineral that had been selectively coated.

This is the basic mechanism of flotation, but it is never that simple in actual practice where ores may be complex and variable and where such things as costs, grade, recovery, smelter penalties and marketability are always uppermost in mill operators' minds. Fortunately, there are many ways available, well understood by flotation experts, to modify this basic process so as to obtain close to optimum results. (1-15)

One such modification is the basis for the work undertaken on this project. It is the use of cyanide in the copper, lead, and zinc milling industries as a depressant for pyrite in the flotation of copper, lead, and zinc minerals. Many of the collectors used in the flotation of these minerals also coat iron sulfide particles, with the result that they too float with the valuable minerals, significantly lowering the grade of concentrates obtained. The use of cyanide has been found to prevent this co-flotation of pyrite.

Aware of the wide use of cyanide in the base-metal mineral industries as a pyrite depressant, EPA engaged Battelle to conduct a two-phase program to determine the feasibility of substituting alternative reagents for cyanide (a priority pollutant).

Phase I of the program was to consist of limited experimental work to identify possible substitutes for cyanide as a pyrite depressant.

Phase II, contingent on the outcome of the Phase I work, was designed originally to determine the practical and economic impact on the industry of a changeover from cyanide to alternate reagents indicated as being feasible by the Phase I work.

The Phase I work indicated that sodium sulfide and sodium sulfite might possibly be satisfactory substitutes for cyanide. In the Phase II program, which involved interviewing the officials and supervisors of seventeen copper, lead, and zinc mills in four states, it was early recognized that it would be impossible in the scope of this effort to quantify the cost of a changeover to alternate reagents. This phase culminated in a recommended plan for establishing such a changeover.

TASK 1. LITERATURE SEARCH

The literature of the period 1968-1978 dealing with pyrite depressants was surveyed using the computer search of these data bases: Chemical Abstracts, Smithsonian, Dissertation Abstracts, Engineering Index, and NTIS (National Technical Information Service). Key words which were used in the broadly defined search were the following: flotation, ore treatment, chalcocite, chalcopyrite, sphalerite, galena, pyrite, depress.

A total of 38 articles relevant to the topic of pyrite depression were identified in the computer search. (A complete listing appears on page A-1, Appendix A.)

A review of the books and articles (see page A-6, Appendix A) acquired had the following objectives:

- Identify substances other than sodium cyanide which have been or may be used as depressants for pyrite.
- Gather information concerning the performance, selectivity, environmental hazards, and economics of the use of such alternatives.

Fourteen candidate depressants were identified. These substances may be grouped into classes as follows:

- Metal salts -- silver, chromium, mercury, copper, aluminum, and iron salts (tested as nitrates in the literature) -- these are thought to produce a complex of collector molecules and metal hydroxides on mineral surfaces, thus preventing collector contact with the mineral (16, 17).

- Reducing agents -- sodium sulfide, sodium thiosulfate, sodium hypophosphite, sodium oxalate, and sodium sulfite (or other soluble salts of the same anions) -- these decrease the oxidation potential of the solution and are preferentially oxidized at the pyrite surfaces (7). Thus they prevent collector oxidation in the bulk solution or at the solution/mineral interface. Without the presence of the oxidized collector, pyrite flotation is inhibited.
- Oxidizing agents -- potassium permanganate, sodium dichromate -- these, on the other hand, act on the pyrite surface to destroy the hydrophobic character of the surface by forming the metal hydroxide.
- Miscellaneous -- Kr6D (lignin derivative) -- the mechanism of pyrite depression is not clear in the case of Kr6D.

Information from the literature on each of the alternative depressants is summarized in Tables B-1 through B-9 in Appendix B. In each case information was sought concerning the depressant's performance on pyrite, selectivity, environmental considerations, economics, and state of development. In addition, the theory of depressant action, when known, was summarized.

Tables B-1 through B-9 also contain comments considered in the evaluation and ranking in the following task.

TASK 2. ASSESSMENT OF ALTERNATIVES TO CYANIDE AS FLOTATION CONTROL REAGENT

The information obtained in the literature search was evaluated to determine three alternative depressants with the best combination of the following attributes:

- Effective pyrite depression
- Selective depressant action (good desired metal recovery)
- Low environmental pollution potential
- Cost per ton of ore processed similar to cyanide
- High state of development as a practical depressant
- Low toxicity.

The approach to the basic assessment strategy was to score each candidate based on possession of the attributes noted above and to rank the depressants according to the scores thus assigned. A reagent was given a "+" rating on performance (see Table 1) if a relatively small reagent concentration produced a high degree of pyrite rejection in flotation tests. A "-" performance

TABLE 1. EVALUATION AND RANKING CRITERIA (a) FOR PYRITE DEPRESSANTS

Attribute	Performance rating	
	+	-
Performance	High pyrite rejection levels, reasonably low depressant concentration required	Low to moderate pyrite rejection levels, high depressant concentration required
Selectivity	No interference with subsequent flotation steps, high recovery of nonpyrite minerals	Interference with subsequent flotation steps, low recovery of nonpyrite minerals
Environmental considerations	Generally considered nonhazardous	Potentially hazardous
Cost considerations (b)	Cost per ton of ore processed similar to cyanide	High cost per ton of ore processed
Developmental status	Used commercially in pilot plant or in extensive laboratory-scale optimization	Subjected to screening tests only

(a) A value of "0" will be assigned to a particular depressant if insufficient information is available for assignment of a "+" or "-" value.

(b) A favorable impact on cost would take into consideration not only the cost of the depressant but also the need and complexity of wastewater treatment if it were used.

TABLE 2. PYRITE DEPRESSANT EVALUATION AND RANKING

Depressant	Performance	(b) Selectivity	Environmental Considerations (b) and Toxicity	Cost Considerations (b)	Developmental Status (b)	Total Evaluation Score	Rank
<u>Heavy Metals</u> (as nitrate salts)							
Ag	+	+	-	-	-	-1	6
Cr(III)	+	-	-	-	-	-3	12
Hg(II)	+	-	-	-	-	-3	12
Cu(II)	-	-	-	-	-	-5	14
Al	-	-	+	+	-	-1	6
Fe(III)	-	-	+	+	-	-1	6
<u>Reducing Agents</u>							
Na ₂ S	+	-	+	+	+	+3	3 (a)
Na ₂ S ₂ O ₃	+	+	+	+	+	+5	1 (a)
NaH ₂ PO ₂	+	0	0	-	-	-1	6
Na ₂ C ₂ O ₄	+	0	-	+	-	0	5
Na ₂ SO ₃	+	+	+	+	+	+5	1 (a)
<u>Oxidizing Agents</u>							
KMnO ₄	+	0	-	-	-	-2	10
Na ₂ Cr ₂ O ₇	+	0	-	-	-	-2	10
<u>Miscellaneous</u>							
Kr6D	0	+	0	0	0	+1	4

(a) Selected for screening study.

(b) Each "+" or "-" has a value of 1.

rating was given if a relatively large reagent concentration was needed to produce a high or low degree of pyrite rejection. If a "+" or "-" rating could not be assigned on the basis of information found in the literature, a "0" rating was given. The other evaluation criteria were treated in the same way, according to the criteria descriptions set forth in Table 1.

After a depressant received ratings on all criteria, the individual +, -, and 0 ratings were added to produce a total evaluation score. When all alternative depressants had received total scores, ranks from 1 through 14 were assigned based on the total evaluation scores.

All the individual criterion scores, total evaluation scores, and ranks are summarized in Table 2 for all of the alternative depressants. For example, sodium sulfite has a total score of "+5", the sum of five "+" ratings for each of the attribute areas. On the other hand, potassium permanganate has a score of "-2", the sum of "-" ratings for environmental hazard, high cost per ton of ore processed, and low developmental status; a "0" rating for insufficient information concerning selectivity; and a "+" rating for good pyrite depression performance. The relative ranks of sodium sulfite and potassium permanganate based on the criteria cited are, as a result, "1" and "10".*

Performance and Selectivity of Pyrite Depressants

A number of pyrite depressants cited in the literature exhibited good performance in depressing pure pyrite, but there are fewer examples of substances which selectively depress pyrite. Among the metal nitrates, in tests using 0.06 lb/ton (0.03 kg/metric ton) potassium ethyl xanthate (KEX) as collector and 0.20 lb/ton (0.10 kg/metric ton) of terpeneol as frother (pH unspecified), pyrite depression was achieved with additions of 0.4 lb (0.2 kg/metric ton) AgNO_3 /ton, 0.8 lb (0.4 kg/metric ton) $\text{Cr}(\text{NO}_3)_3$ /ton, 1.0 lb (0.5 kg/metric ton) $\text{Hg}(\text{NO}_3)_2$ /ton, 4.0 lb (2.0 kg/metric ton) $\text{Al}(\text{NO}_3)_3$ /ton, or 7.0 lb (3.5 kg/metric ton) $\text{Fe}(\text{NO}_3)_3$ /ton (18). Thus silver, chromium (III), and mercury (II) salts exhibit good performance in pyrite depression; however, additions less than 0.2 lb (0.1 kg/metric ton) $\text{Cr}(\text{NO}_3)_3$ /ton and 4 lb (2 kg/metric ton) $\text{Hg}(\text{NO}_3)_2$ /ton under similar conditions completely depress galena; and less than 1 lb (0.5 kg/metric ton) $\text{Cr}(\text{NO}_3)_3$ /ton completely depresses chalcocite. Silver is considerably more sensitive than Cr (III) and Hg (II) in that a 5-lb (2.27 kg) AgNO_3 addition depresses only 58 percent of a galena sample (18). In short, soluble salts are the only metallic salts which combine performance and selectivity. Their cost, however, is high and will remain so.

The reducing salts sodium sulfide (Na_2S), sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$), sodium hypophosphite (NaH_2PO_2), sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$), and sodium sulfite (Na_2SO_3) are all good pyrite depressants in conformance with the theory that reduction of solution oxidation potential depresses pyrite by preventing xanthate oxidation. At pH 10, 2×10^{-4} additions of Na_2S , $\text{Na}_2\text{S}_2\text{O}_3$, NaH_2PO_2 , $\text{Na}_2\text{C}_2\text{O}_4$, and Na_2SO_3 , respectively, yielded pyrite depressions of 100, 98, 98, 95, and 100 percent (7). Less information is available concerning the

* The need for more data here is obvious and, once more information is available, rankings and criteria for ranking are expected to change.

selectivity of these substances as pyrite depressants. Sodium sulfide has been shown to have poor selectivity toward pyrite depression in the presence of galena, chalcocite, and chalcopyrite (19). No information was found on selectivity of sodium oxalate and hypophosphite. Sodium thiosulfate exhibits good pyrite depression selectivity over copper and lead minerals, but poor selectivity over sphalerite (22). The depression of ZnS by sodium thiosulfate may not be a disadvantage, since it parallels the behavior of sodium cyanide. Finally, sodium sulfite is highly selective in depression of pyrite over depression of chalcopyrite.

Little information on the performance and no information on the selectivity of potassium permanganate or sodium dichromate is available in the references reviewed. One source simply stated that these two oxidizing agents are among the best pyrite depressants (23). Thus, KMnO_4 and $\text{Na}_2\text{Cr}_2\text{O}_7$ were given positive ratings on performance and "0" ratings (insufficient information available) on selectivity.

The new patented lignin derivative, Kr6D, is a case where information is strictly limited, but what is available is encouraging. The substance is a mixture of a soluble polymer, sodium carboxymethylcellulose, and a soluble lignosulfonate salt, sodium or calcium lignosulfonate. Kr6D has been shown to completely depress galena and sphalerite at concentrations as low as 10 ppm and 5 ppm, respectively, while requiring 100 ppm for chalcopyrite depression (24, 25). Thus, selectivity against chalcopyrite depression has been demonstrated, but performance on pyrite is unknown.

Environmental Considerations

There is little or no published information concerning the environmental aspects of alternatives to cyanide. Thus, it was necessary to evaluate the alternative reagents without the benefit of data from the literature on environmental aspects of the problem.

Rather than assigning "0" (insufficient information) values to all candidate depressants in the environmental part of the evaluation process, it was decided that most of the reagents could be assigned "hazardous" or "nonhazardous" ratings on the basis of common knowledge. Such a grouping, although not a rigorous comparison of the environmental hazards of the materials, would be preferable to an assumption that all of the depressants are equal in this regard.

The heavy metals, silver, chromium, mercury, and copper were given a "-" (hazardous) rating on the basis of the commonly known toxicity of the soluble cations (only soluble metal salts would be useful as flotation reagents) of the metals, and the carcinogenic properties of certain chromium compounds in particular. On the other hand, the metals aluminum and iron were rated "+" (nonhazardous) on the basis of their easy removal from solution.

Of the five reducing agents which were considered, only one was given a "-" rating: sodium oxalate, due to its toxicity. Sodium sulfide, thiosulfate, and sulfite were rated "+". Although all of the reducing agents would be associated with high chemical oxygen demand (COD), the quantities which would be released from the flotation process should be much too small to have a significant effect. Sodium sulfide would release toxic H_2S gas if exposed to an acidic solution. Since any Na_2S released with tailings would be exposed to dissolved heavy metals, residual Na_2S could be precipitated as metal sulfides. The degree of hazard associated with the use of sodium hypophosphite is not commonly known.

Both oxidizing agents, potassium permanganate and sodium dichromate, were given a "-" rating because they contain the heavy metals manganese and chromium. Although little information is available concerning the dosages of these reagents needed for pyrite depression, it was assumed that hazardous quantities could be released from a flotation plant, even if only in abnormal plant operation.

Since Kr6D is a new commercial product, no judgment of its environmental hazards could be made. A "0" rating was thus assigned to Kr6D in the environmental phase of evaluation, denoting the total lack of published information on Kr6D toxicity in the minerals processing literature.

Economic Considerations

The economics of reagent used received no attention in the recent literature review. As in the case of the environmental evaluation, the lack of specific information in the literature requires that the candidate depressants be classified as high or low cost per ton of ore processed, on the basis of common knowledge of the cost of reagents. Rated as low cost per ton of ore processed are the following: iron and aluminum salts, sodium sulfide, sodium thiosulfate, sodium oxalate, and sodium sulfite. High cost reagents are as follows: silver, chromium, mercury, and copper salts, sodium hypophosphite, potassium permanganate, and sodium dichromate. Nothing is known about the cost of lignin derivatives such as Kr6D.

Development Status

According to the literature reviewed, very few of the alternative depressants have been extensively tested or used commercially. Sodium sulfide and sodium sulfite both have been used commercially. Sodium thiosulfate has been tested for performance and selectivity more extensively than the other depressants, although no references to its commercial use were found in the literature. Thus, these three alternatives received "+" ratings.

Little is known concerning the development status of Kr6D. The manufacturer has tested it on ores containing galena, sphalerite, chalcopryrite, and molybdenite, and states that customers have tested it on other ores (27). The lack of information earns Kr6D a "0" rating in this category.

No references to extensive testing or use of any of the other depressants were found. Thus, all of the remaining alternative reagents received a "-" rating on developmental status.

Selection of the Most Promising Alternative Pyrite Depressants

The three reagents with the highest ranking in the evaluation are sodium sulfide, sodium thiosulfate, and sodium sulfite, with respective evaluation scores of +3, +5, and +5. Sodium cyanide, evaluated according to the same criteria, would have a total evaluation score of +3 and a rank of 3. Thus, these three reducing agents are selected as the most promising alternatives to cyanide as a pyrite depressant. They were the three reagents to be compared to cyanide in laboratory tests of performance and selectivity on three different ore types.

Recommended Additional Data Acquisition and Research

Kr6D ranked fourth in the evaluation (+1, rank = 4). Because the lack of published information on this reagent is primarily responsible for its poor showing, new information as it becomes available may well change its standing. As a natural product, used in low concentrations (5-100 ppm), it may well prove to be economical. It has already been demonstrated to be an effective galena and sphalerite depressant, with selectivity against chalcopyrite, and may well be an effective pyrite depressant. Thus, it would be wise, when more funding becomes available, to attempt to fill the data gaps concerning Kr6D, especially in regard to its performance on pyrite and its environmental effects.

None of the other alternatives appear to be worth looking more closely at individually, as each has overall limitations as a pyrite depressant. Several, however, may have utility in combination with other more effective reagents. For example, the use of Kr6D in combination with either sodium dichromate or SO_2 has improved the grade of a copper concentrate over that produced by Kr6D alone (25). This and other symbiotic effects of two or more reagents ought to be studied carefully.

TASK 3. LABORATORY STUDIES

The three pyrite depressants selected for comparison with sodium cyanide were sodium sulfide, sodium thiosulfate, and sodium sulfite. A domestic chalcopyrite ore, a copper-lead-zinc ore, and a zinc ore were used in the study.

The chalcopyrite ore sample was a rod-mill feed with about 4.3 percent moisture and had the size distribution given in Table 3. The rod-mill feed of the copper-lead-zinc ore (4.5 percent moisture) was slightly finer. The zinc ore was significantly finer (see Table 3) and generally dustier than the other two ores. The zinc ore was considered to be a product from a rod mill rather than the feed to the mill, although its origin was not specified.

The ores were reduced in size by wet ball milling just before each flotation test (500 g minus 1/4-inch ore, 750 ml H₂O, 8025 g steel balls). The grinding period was determined experimentally in a single experiment with the target being 65 percent minus 200 mesh. The results given in Table 4 suggested that each of the grinding times had to be reduced 5 minutes for the samples to be froth floated.

Sample and Reagent Preparation

Each ore sample was coned and quartered to split out a head sample and the remainder divided into 20 representative samples, each containing approximately 500 g ore. Fresh collector solution was prepared just before each flotation with distilled water at a concentration of 1.25 percent by weight because the xanthate solution oxidizes easily. In addition, solutions of the selected depressants were prepared with distilled water at the molar concentrations needed for the flotation study.

Experimental Conditions

With each ore sample, a series of froth flotation experiments was carried out to evaluate the performance of the selected depressants. Additional flotation runs were made without using any depressant and with sodium cyanide to provide baseline data for comparison. Depressant concentration and the pH were varied at two levels. Remaining variables such as pulp density, rotation speed, retention time, and air flow rate were held constant.

The fixed conditions for the batch flotation experiments were as follows:

- Collector -- KEX @ 1 ml of 1.25 weight percent solution
- Frother -- Aerofrother 65 @ 3 drops
- Pulp density -- 20 weight percent (i.e., 500 g ore in 2000 ml distilled water)
- Agitator speed -- 1000 rpm
- Retention time -- 8-min conditioning and 8-min floating
- Air flow rate -- natural suction.

TABLE 3. DRY SIEVE ANALYSIS OF AS-RECEIVED ORES

Mesh Size, Tyler	Percent by Weight	
	Fraction	Cumulative
<u>Chalcopyrite Ore</u>		
+1/2"	5.2	5.2
1/2" x 1/4"	22.3	27.5
1/4" x 14	47.4	74.9
14 x 20	5.1	80.0
20 x 28	4.3	84.3
28 x 35	3.6	87.9
35 x 48	3.6	91.5
48 x 65	2.5	94.0
65 x 100	2.2	96.2
-100	3.8	100.0
<u>Copper-Lead-Zinc Ore</u>		
+1/2"	8.4	8.4
1/2" x 1/4"	22.8	31.2
1/4" x 14	37.1	68.3
14 x 20	4.5	72.8
20 x 28	3.6	76.4
28 x 35	3.1	79.4
35 x 48	3.4	82.9
48 x 65	2.7	85.6
65 x 100	3.1	88.7
-100	11.3	100.0
<u>Zinc Ore</u>		
+1/2"	0	0
1/2" x 1/4"	1.3	1.3
1/4" x 14	43.5	44.8
14 x 20	6.5	51.3
20 x 28	6.0	57.3
28 x 35	6.1	63.4
35 x 48	5.9	69.3
48 x 65	5.5	74.8
65 x 100	4.7	79.5
-100	20.9	100.4

TABLE 4. WET SIEVE ANALYSIS OF BALL-MILLED ORES

Mesh Size, Tyler	Percent by Weight	
	Fraction	Cumulative
<u>Chalcopyrite, 25-min grind</u>		
+65	0.5	0.5
65 x 100	1.0	1.5
100 x 150	3.3	4.8
150 x 200	8.7	13.5
200 x 270	9.4	22.9
270 x 325	7.8	30.7
-325	69.3	100.0
<u>Copper-Lead-Zinc Ore, 25-min grind</u>		
+65	0.8	0.8
65 x 100	0.6	1.4
100 x 150	3.0	4.4
150 x 200	6.8	11.2
200 x 270	7.9	19.1
270 x 325	10.5	29.6
-325	70.4	100.0
<u>Zinc Ore, 20-min grind</u>		
+65	0.25	0.25
65 x 100	1.05	1.30
100 x 150	4.19	5.49
150 x 200	12.01	17.50
200 x 270	9.41	26.90
270 x 325	9.76	36.67
-325	63.34	100.01

Except for the zinc ore sample, 18 batch flotation runs were made at the experimental conditions shown in Table 5. Results from the first two experiments suggested that only the 12 experiments noted as (d) needed to be carried out on the zinc ore.

Experimental Procedure

The experimental procedure for batch flotation experiments was as follows, except where otherwise stated:

- (1) Place 500 g of the ore sample in the flotation cell and add 2000 ml of distilled water
- (2) Add the prepared depressant solution to obtain the pre-determined concentration, i.e., 10^{-5} M or 10^{-3} M
- (3) Add 0.5 g of CaO
- (4) Agitate the slurry for 5 min at a speed of 1000 rpm without aeration
- (5) Measure the pH of the slurry
- (6) Add 1 ml of the collector solution (1.25 weight percent KEX) and agitate 3 min without aeration
- (7) Add three drops of Aerofroth 65 and turn the air on
- (8) Collect froth product for 8 min
- (9) Turn off the agitator and skim off the remaining froth product
- (10) Filter both froth product and tailings separately
- (11) Dry the filter cakes overnight in an oven at about 100°C
- (12) Weigh the dried cakes and send for analysis.

Chemical Analysis and Performance Evaluation

Both froth product and tailings from each flotation run were analyzed for their metal contents: i.e., Fe and Cu for the copper ore; Fe and Zn for the zinc ore; and Fe, Cu, Pb, and Zn for the copper-lead-zinc ore. The three ore head samples were also analyzed for their metal contents.

The flotation results were evaluated in terms of the following parameters:

$$\text{Total Weight Recovery (\%)} = \frac{\text{Wt of Product}}{\text{Wt of Product} + \text{Wt of Tailings}} \times 100$$

TABLE 5. EXPERIMENTAL CONDITIONS FOR BATCH FLOTATION EXPERIMENTS

Run No.	Depressant		pH Adjustment
	Type	Concentration, M	
1 ^(d)	None	--	Neutral (a)
2 ^(d)	None	--	CaO(b)
3 ^(d)	NaCN	10 ⁻⁵	Neutral or >7 ^(c)
4 ^(d)	NaCN	10 ⁻⁵	CaO
5 ^(d)	NaCN	10 ⁻³	Neutral or >7
6 ^(d)	NaCN	10 ⁻³	CaO
7 ^(d)	Na ₂ S	10 ⁻⁵	Neutral
8 ^(d)	Na ₂ S	10 ⁻⁵	CaO
9	Na ₂ S	10 ⁻³	Neutral
10	Na ₂ S	10 ⁻³	CaO
11 ^(d)	Na ₂ SO ₃	10 ⁻⁵	Neutral
12 ^(d)	Na ₂ SO ₃	10 ⁻⁵	CaO
13 ^(d)	Na ₂ SO ₃	10 ⁻³	Neutral
14 ^(d)	Na ₂ SO ₃	10 ⁻³	CaO
15	Na ₂ S ₂ O ₃	10 ⁻⁵	Neutral
16	Na ₂ S ₂ O ₃	10 ⁻⁵	CaO
17	Na ₂ S ₂ O ₃	10 ⁻³	Neutral
18	Na ₂ S ₂ O ₃	10 ⁻³	CaO

(a) The pH of the slurry was not adjusted.

(b) The pH was raised by adding 0.5 g of fresh CaO.

(c) With NaCN the pH of the slurry was kept above 7 by adding NaOH if necessary.

(d) Conditions used in the 12 zinc ore experiments.

$$\text{Metal* Recovery} = \frac{(\% \text{ Metal in Product})(\text{Wt of Product}) \times 10^3}{(\text{kg/metric ton of ore})(\text{Initial Sample Weight})}$$

Results

Chalcopyrite Ore (Cu = 0.73; Fe = 4.51 percent)--

Eighteen flotations were performed on a freshly ground copper ore (at least 65 percent minus 200 mesh) using the selected depressants, sodium cyanide, and no depressants as described in the experimental procedures above. The odd numbered experiments listed in Table 6 were performed at natural pH while the even numbered experiments were treated with a fixed amount of lime to raise the pH.

The results in Table 6 show that under the conditions of these experiments copper recovery at both natural and high pH was 4.6 and 4.22 kg/tonne, respectively, when NaCN (10^{-3} M) was used as a pyrite depressant. Copper recovery attained with NaCN was matched or surpassed using Na_2S (Experiments 9 and 10 at 5.07 and 4.98 kg/tonne, and Na_2SO_3 (Experiments 16 and 18 at 4.68 and 5.23 kg/tonne). However, the level of pyrite depression, as measured by the Cu to Fe weight ratio in the float fraction (Cu:Fe of 0.67 to 0.85) obtained by NaCN only approached that of the Na_2SO_3 (Experiment 13 where Cu:Fe = 0.68).

Copper-Lead-Zinc Ore (Cu = 0.54; Pb = 4.75; Zn = 7.98; Fe = 4.50 percent)--

The results from the 18 experiments on a copper-lead-zinc ore employing the same experimental conditions used for the copper ore are given in Table 7. In Experiments 3A, 4A, 5A, and 6A in which NaCN was used, copper recoveries were 4.20, 3.66, 3.97, and 3.00 kg/tonne (3.77 avg); lead recoveries were 38.7, 50.5, 37.5, and 34.0 kg/tonne (40.2 avg); and zinc recoveries were 27.5, 34.9, 17.7, and 17.1 kg/tonne (24.3 avg). For copper, equal or greater recoveries were obtained with each of the pyrite depressants and at each of the concentrations studied. The effectiveness of the depressant, as measured by comparing the Cu:Fe ratios of the froth fractions with those obtained using NaCN (Cu:Fe of 0.52 to 0.63), was only approached using Na_2S (Experiment 8 at 0.47) and Na_2SO_3 (approached in Experiments 11 at 0.56 and 14 at 0.48 and exceeded in Experiment 13 at 0.62). For lead, recoveries obtained with each of the pyrite depressants and concentrations equaled or surpassed that attained using NaCN. The effectiveness of the depressant, as measured by the Pb:Fe weight ratio in the froth fraction obtained using NaCN (Pb:Fe of 5.80 to 7.16), was approached using Na_2S (Experiment 8 at 4.17) and Na_2SO_3 (Experiments 11 at 5.49, 13 at 4.91, and 14 at 4.64).

In beneficiation of a copper-lead-zinc ore by froth flotation it is often desirable to suppress the flotation of zinc during the initial separation of copper and lead. In this study, it is assumed that this is a desired effect and low values for zinc recovery and Zn:Fe are sought as well as a high recovery and ratios for copper and lead. With this as an added criterion for the evaluation of performance of depressants, Na_2SO_3 (Experiments 11 at 2.99, 13 at 1.78, and 14 at 2.49) exhibits this characteristic and equals or surpasses the performance of NaCN (Experiments 3A, 4A, 5A, and 6A with Zn:Fe of 2.79 to 4.96).

* The metal represents Fe, Cu, Zn, or Pb.

TABLE 6. CHALCOPYRITE ORE RESULTS

Exp.	Type Depressant	Conc., M	pH	Sample Weight, gm		Product Recovery, %	Tailings Analysis, Cu, % Fe, %		Cu in Product		Fe in Product
				Initial	Product		Cu, %	Fe, %	%	gm	%
										kg/tonne	kg/tonne
1 (a)	None	--	7.8	500.0	44.4	8.87	0.45	3.04	3.97	1.76	3.52
2 (b)	None	--	11.0	501.1	20.5	4.09	0.47	2.69	8.44	1.73	3.45
3	NaCN	10 ⁻⁵	8.0	500.9	32.6	6.51	0.49	3.04	3.94	1.28	2.56
4	NaCN	10 ⁻⁵	11.0	502.2	24.8	4.93	0.30	2.55	6.40	1.59	3.17
5	NaCN	10 ⁻³	8.5	504.0	29.9	5.93	0.30	3.05	7.77	2.32	4.60
6	NaCN	10 ⁻³	10.9	497.8	47.9	9.62	0.30	3.31	4.39	2.10	4.22
7	Na ₂ S	10 ⁻⁵	8.5	503.9	40.7	8.08	0.47	2.95	3.90	1.59	3.16
8	Na ₂ S	10 ⁻⁵	10.8	507.8	54.2	10.67	0.32	2.31	3.69	2.00	3.94
9	Na ₂ S	10 ⁻³	8.0	505.2	69.6	13.78	0.26	2.57	3.68	2.56	5.07
10	Na ₂ S	10 ⁻³	11.0	506.0	38.6	7.63	0.26	2.46	6.54	2.52	4.98
11	Na ₂ SO ₃	10 ⁻⁵	8.2	504.0	30.6	6.07	0.52	3.19	4.96	1.52	3.02
12	Na ₂ SO ₃	10 ⁻⁵	10.9	504.8	25.0	4.95	0.42	2.62	7.86	1.97	3.90
13	Na ₂ SO ₃	10 ⁻³	8.3	497.4	30.4	6.10	0.34	2.94	6.81	2.07	4.16
14	Na ₂ SO ₃	10 ⁻³	10.9	504.9	44.2	8.79	0.29	2.38	5.23	2.31	4.59
15	Na ₂ S ₂ O ₃	10 ⁻⁵	8.2	501.9	22.9	4.56	0.40	2.77	7.02	1.61	3.21
16	Na ₂ S ₂ O ₃	10 ⁻⁵	11.0	501.7	41.1	8.19	0.27	2.58	5.71	2.35	4.68
17	Na ₂ S ₂ O ₃	10 ⁻³	8.5	503.5	23.0	4.57	0.39	2.65	7.71	1.77	3.52
18	Na ₂ S ₂ O ₃	10 ⁻³	11.1	500.8	39.6	7.91	0.18	2.14	6.62	2.62	5.23

(a) All odd-numbered experiments are natural pH with no pH adjustment.

(b) In all even-numbered experiments the pH was adjusted with 0.5g CaO; pH before depressant addition.

(c) kg/tonne = kilogram per metric ton of ore.

TABLE 7. COPPER-LEAD-ZINC ORE RESULTS

Exp.	Type Depressant	Conc., M	pH	Sample Weight, gm		Product Recovery, wt. %	Tailings Analysis			Cu In Product, gm/kg/tonne ore (c)	Fe In Product, gm/kg/tonne ore (c)	Pb In Product, gm/kg/tonne ore (c)	Zn In Product, gm/kg/tonne ore (c)										
				Initial Product	Tailings		Cu, %	Fe, %	Pb, %					Zn, %									
1A (a)	None	--	7.9	495.1	59.4	435.7	12.0	0.16	3.96	1.14	6.05	3.12	1.85	3.74	6.15	3.65	7.38	31.0	18.4	37.2	17.5	10.50	21.1
2A (b)	None	--	10.9	500.9	67.0	433.9	13.4	0.14	4.28	1.18	4.98	3.24	2.17	4.33	6.12	4.10	8.19	26.6	17.8	35.6	21.0	14.10	28.1
3A	NaCN	10 ⁻⁵	7.8	498.8	61.2	437.6	12.3	0.15	4.29	1.16	5.58	3.42	2.09	4.20	5.44	3.33	6.67	31.5	19.3	38.7	22.4	13.20	27.5
4A	NaCN	10 ⁻⁵	10.7	509.5	80.4	429.1	15.6	0.20	4.47	1.38	3.42	2.32	1.87	3.66	4.46	3.59	7.04	32.0	25.7	50.5	22.1	17.80	34.9
5A	NaCN	10 ⁻³	7.9	505.3	55.1	450.2	10.9	0.16	4.28	1.13	6.95	3.64	2.01	3.97	5.81	3.20	6.34	34.4	19.0	37.5	16.2	8.93	17.7
6A	NaCN	10 ⁻³	10.8	507.6	51.8	455.8	10.2	0.24	4.31	1.26	6.46	2.94	1.52	3.00	5.46	2.83	5.57	33.3	17.3	34.0	16.8	8.70	17.1
7A	Na ₂ S	10 ⁻⁵	7.8	510.9	64.5	446.4	12.6	0.20	4.84	1.20	7.20	4.18	2.70	5.28	7.81	5.04	9.86	32.6	21.0	41.2	15.4	9.93	19.4
8A	Na ₂ S	10 ⁻⁵	10.6	505.0	66.1	438.9	13.1	0.15	4.70	1.17	4.27	2.75	1.82	3.60	5.84	3.86	7.64	24.4	16.1	31.9	24.8	16.40	32.5
9A	Na ₂ S	10 ⁻³	8.6	495.8	68.6	427.2	13.8	0.17	3.53	0.86	6.68	2.73	1.87	3.78	10.00	6.06	13.80	27.1	18.6	37.5	16.6	11.40	23.0
10A	Na ₂ S	10 ⁻³	11.2	499.6	64.0	435.6	12.8	0.14	3.91	0.84	5.66	3.03	1.94	3.88	7.08	4.53	9.07	26.1	16.7	33.4	19.2	12.30	24.6
11A	Na ₂ SO ₃	10 ⁻⁵	7.9	499.2	53.2	446.0	10.7	0.14	3.92	0.96	6.19	3.37	1.79	3.59	5.95	3.17	6.34	32.7	17.4	34.9	17.8	9.67	19.0
12A	Na ₂ SO ₃	10 ⁻⁵	10.6	498.3	90.8	407.5	18.2	0.10	3.96	1.10	2.49	2.11	1.92	3.84	6.17	5.60	11.20	26.3	23.9	47.9	24.2	22.00	44.1
13A	Na ₂ SO ₃	10 ⁻³	7.4	504.4	46.0	458.4	9.1	0.15	4.88	1.17	6.15	4.40	2.02	4.01	7.08	3.26	6.46	34.8	16.0	31.7	12.6	5.80	11.5
14A	Na ₂ SO ₃	10 ⁻³	10.7	501.9	60.0	441.9	12.0	0.15	4.58	1.01	5.89	3.17	1.90	3.79	6.54	3.92	7.82	30.3	18.2	36.2	16.3	9.78	19.5
15A	Na ₂ O ₂ ·3H ₂ O	10 ⁻⁵	7.7	502.4	64.8	437.6	12.9	0.12	4.47	0.94	5.50	3.28	1.19	4.23	7.06	4.57	9.11	30.6	19.8	39.5	19.6	12.70	25.3
16A	Na ₂ O ₂ ·3H ₂ O	10 ⁻⁵	10.6	497.9	80.4	437.5	16.2	0.08	4.28	0.77	1.79	2.37	1.91	3.83	6.11	4.91	9.87	18.9	15.2	30.5	26.9	21.60	43.4
17A	Na ₂ S ₂ O ₃	10 ⁻³	7.8	501.8	67.7	436.1	13.5	0.12	3.91	0.91	5.51	3.09	2.09	4.17	5.91	4.00	7.97	27.2	18.4	36.7	21.0	14.20	28.3
18A	Na ₂ S ₂ O ₃	10 ⁻³	10.6	503.4	63.5	439.9	12.6	0.14	3.88	1.08	5.82	2.92	1.85	3.68	5.93	3.77	7.48	27.9	17.7	35.2	17.5	11.10	22.1

All odd-numbered experiments are natural pH with no pH adjustment.

(a) All odd-numbered experiments are natural pH with no pH adjustment.

(b) In all even-numbered experiments the pH was adjusted with 0.5 M CuO.

(c) kg/tonne = kilogram per metric ton of ore.

Zinc Ore (Zn = 7.09; Fe = 8.15 percent)--

Based on the results of the zinc fraction from the copper-lead-zinc ore experiments, only the behavior of sodium sulfite and sodium sulfide as depressants was examined (only the 10^{-5} M concentration of sodium sulfide was used). The results of 12 experiments using zinc ore are given in Table 8. The experiment numbering sequence is identical to that used for the previous ores and that outlined in the experimental procedure in Table 5. The results suggest that zinc recovery using NaCN at both natural and high pH was about 1.52 kg/tonne at 10^{-5} M and between 1.1 and 1.2 kg/tonne at 10^{-3} M. Both these values were lower than the 1.59 to 1.68 kg/tonne zinc recovery obtained when a depressant was absent. Zinc recovery attained with NaCN was surpassed using 10^{-5} M Na_2S (Experiments 7B at 1.87 kg and 8B at 1.96 kg/tonne), and Na_2SO_3 (Experiments 11B at 1.52, 12B at 1.88, and 14B at 1.78 kg/tonne). The level of pyrite depression obtained as measured by the Zn to Fe ratio in the float fraction was greatest with 10^{-5} M Na_2S (Experiment 8B at Zn:Fe 1.28), and 10^{-3} M Na_2SO_3 (Experiment 14B at Zn:Fe 1.21). These ratios are just slightly better than those obtained when no depressant was used (Experiment 2B at Zn:Fe 1.22) or when NaCN was used. The fact that sphalerite (ZnS ore) is one of the most difficult of the sulfide ores to float is reflected in these experiments. Known techniques used to improve the floatability of zinc ores (such as the addition of soluble copper salts to the system) were not used in these depressant screening experiments. Since the goal of the experiments was to demonstrate rejection of pyrite in the float, the conditions used were judged to be a more severe test of the reagent performance.

CONCLUSIONS

The results from these preliminary screening experiments suggest that sodium sulfide, Na_2S , and sodium sulfite, Na_2SO_3 , could approach the effectiveness of sodium cyanide, NaCN, as a pyrite depressant under the constraints of this experimental program and the ores studied. The results suggest that their use should be evaluated as an alternative to the treatment of large volumes of mining wastewater containing low concentrations of cyanide. The breadth of applicability of such alternative depressants remains unknown and must be determined. The benefits of reduced environmental effects must be weighed against possible effects on processing the continually leaner sulfide ore bodies adaptable to beneficiation by froth flotation. Losses of metal value to tailings or the misplacement of metal values into the beneficiated ore due to less selective flotation separations also may produce undesirable environmental and economic effects. Therefore, any displacement of optimized beneficiation processes based on the use of sodium cyanide as a depressant by one using an alternative pyrite depressant can have a substantial impact on an important sector of the mining industry.

TABLE 8. ZINC ORE RESULTS

Exp.	Type Depressant	Conc., M	pH	Sample Weight, gm Initial Product Tailings	Product Recovery, Wt. %	Tailings Analysis Zn, % Fe, %	Zn in Product % gm kg/tonne (c)	Fe in Product % gm kg/tonne (c)
1B (a)	None	--	8.5	487.2 18.43 397.4	89.8	8.24 8.71	4.21 0.78	5.67 1.04 2.14
2B (b)	None	--	10.8	491.7 16.78 409.2	82.5	7.87 9.29	4.93 0.83	4.07 0.68 1.39
3B	NaCN	10 ⁻⁵	8.5	490.7 16.24 411.0	79.7	7.78 9.31	3.87 0.63	4.11 0.67 1.36
4B	NaCN	10 ⁻⁵	10.8	493.0 16.06 413.8	79.2	7.94 8.88	4.16 0.67	3.73 0.60 1.22
5B	NaCN	10 ⁻³	8.6	491.7 16.37 411.2	80.5	8.43 8.98	3.73 0.61	3.30 0.54 1.10
6B	NaCN	10 ⁻³	11.0	494.6 14.56 422.6	72.0	7.95 9.05	3.67 0.53	3.71 0.54 1.09
7B	Na ₂ S	10 ⁻⁵	9.0	492.1 21.44 386.6	105.5	8.17 8.95	4.31 0.92	6.11 1.31 2.65
8B	Na ₂ S	10 ⁻⁵	11.0	494.9 18.02 405.7	89.2	7.82 9.83	5.38 0.97	4.21 0.76 1.53
11B	Na ₂ SO ₃	10 ⁻⁵	8.6	491.7 17.94 403.5	88.2	6.95 8.77	4.16 0.75	3.89 0.70 1.42
12B	Na ₂ SO ₃	10 ⁻⁵	10.8	493.4 17.92 405.0	88.4	7.50 9.15	5.19 0.93	4.37 0.78 1.59
13B	Na ₂ SO ₃	10 ⁻³	8.7	492.8 19.46 396.9	95.9	7.85 9.33	4.42 0.86	4.06 0.79 1.60
14B	Na ₂ SO ₃	10 ⁻³	10.8	491.8 17.81 404.2	87.6	7.19 9.04	4.91 0.87	4.05 0.72 1.47

(a) All odd-numbered experiments are natural pH with no pH adjustments.

(b) In all even-numbered experiments the pH was adjusted with 0.5g CaO.

(c) kg/tonne = kilogram per metric ton of ore.

PHASE II INDUSTRY FEEDBACK

The initial phase of the study was concerned with an evaluation of the technical effectiveness of reagents which might be used to replace sodium cyanide for pyrite depression during the flotation of sulfide ores. The results of that effort identified sodium sulfite and sodium sulfide as the most promising candidate alternative suppressants.

To obtain further information on the feasibility of using these reagents it seemed logical to determine from the nonferrous metals industry if they had ever been used or considered for use for this purpose and to determine the economic impact of substituting either of them for sodium cyanide in milling circuits to decrease any adverse environmental effects that continued use of cyanide may have. As the second phase of the study Battelle-Columbus proposed to visit at least twelve mills which process copper, lead, and zinc sulfide ores. During these visits relevant information was to be sought on the effects of the use of alternative pyrite suppressants on the grade of the concentrates, production rates, recoveries, and reagent usage.

The primary objective of this survey was to determine the economic aspects of changing from sodium cyanide to one of the alternative reagents. On an individual basis the cost of (1) the changeover and (2) the long-term use of the alternative reagent were to be determined if at all possible. Early in this phase it became clear that definitive data on the practical and economic feasibility of substituting other reagents for cyanide could not be obtained by the interview and inspection technique. Accordingly, the approach had to be modified to obtain enough information for framing a plan that would eventually permit realization of the original objectives.

The procedure used by Battelle, the findings made, and the conclusions and recommendations arising from the study are presented in this segment of the report.

METHOD OF INVESTIGATION

During Phase II of the study members of the Battelle staff visited eleven companies which operated 17 mills treating copper, copper-lead-zinc, and zinc sulfide ores in Arizona, Utah, Missouri, and Tennessee. The visits were carried out during the period of October 29 to November 9, 1979. Table C-1 in Appendix C provides an alphabetical listing of the companies visited, the state in which the mill is located, and their principal products.

At each site visited, the objectives of the study were explained to the company official after which discussions were held concerning information requested to complete the form shown in Table C-2, Appendix C.

The form has space to record the name of the parent company, the designation and location of the subject mill, the name of the contact, and his title. It provided for the entry of production data (feed tonnage and grade, concentrate tonnages and grade, recoveries, cyanide usage, point of addition of cyanide, purpose of cyanide addition, and the amount of cyanide used per ton of ore processed). Also covered were the daily volume of the wastewater discharged to waters of the state, the concentration of cyanide in the discharge, the mode of occurrence of cyanide in the discharge (thiocyanate, cyanate, ferricyanide, free cyanide, etc.) if known, the cost of the cyanide, whether the mill had an end-of-pipe cyanide destruction process, whether the company had an NPDES permit, and, if so, the cyanide limitation and the company's ability to comply with the provisions of the permit.

Topics for discussion also included on the form were

- The company's experience, if any, with Na_2SO_3 or Na_2S , etc. as pyrite depressants.
- The company's opinion of the technical and economic feasibility of using alternative depressants.
- The company's best judgement of how long it would take to change over to an alternative depressant, assuming that laboratory tests indicated the technical feasibility of so doing.
- Any comments on the economic feasibility of changing over.

ITEMS OBTAINED ON THE VISITS

Tables D-1 through D-15 in Appendix D present the data obtained during the visits. Also presented in Appendix D are summaries of the data and the results of the discussions held with the company representatives. The sections are grouped by states. Plants are designated alphabetically to preserve the anonymity requested by many of the contacts. The alphabetical designation is shown in Table C-1, Appendix C. In some cases two or more plants are grouped in sections. This is because the same contact spoke for more than one mill operating in the immediate area.

Western Mills

Four plants in Southern Arizona and three in Utah were visited. All of these were predominantly copper producers, but virtually all produced by-products (Au, Ag, Mo, etc.). The information they furnished is presented individually in Tables D-1 through D-5 of Appendix D. The Arizona copper mills did not use cyanide as a depressant for pyrites.

Missouri Mills

Officials from three companies which operate six mills in Missouri were interviewed. All of these mills were primarily lead and zinc producers, with copper being a relatively minor by-product. During these visits it was determined that, contrary to the operation of the Arizona copper mills, virtually all of the Missouri mills used cyanide as a depressant for pyrites. Their flotation circuits were much more difficult to operate and sensitive to upsets. The data sheets for these mills are found in Tables D-6 through D-11 in Appendix D as are discussions of the individual operations.

Tennessee Mills

Tables D-12 through D-15 in Appendix D present the data obtained from three companies which operate four mills in Tennessee. Three of these mills were producers of zinc concentrates and the fourth mill produced primarily an iron oxide product with copper and zinc as coproducts. They are also discussed individually in Appendix D as Companies N, O, P, and Q.

It was determined from these visits that when cyanide was used to depress pyrites in zinc ores it was used at near starvation levels (~ 0.02 lb per ton [0.0091 kg/metric ton] of ore processed). Cyanide is not being used in any of the mills now, but one zinc ore mill which is anticipating closing its mill circuit plans to return to the use of cyanide to improve the grade (lower pyrite content). The iron oxide producer uses about 0.1 lb of cyanide per ton (0.045 kg/metric ton) of ore processed for copper recovery because of the high pyrite/pyrrhotite content of the ore.

SUMMARY OF RESULTS FROM THE SURVEY

The results of the survey indicated the following:

- (1) None of the six mills visited or contacted by phone in Arizona (all copper producers) use cyanide or sulfite to depress the flotation of iron sulfides, and none discharged to waters of the state or operated under NPDES permits.
- (2) Most of the Arizona plants use cyanide for the separation, by flotation, of molybdenum sulfide from the copper molybdenum concentrates. This particular use of cyanide was not addressed in this study.
- (3) One large copper producer in Utah was found to use cyanide to depress pyrite flotation, discharged to waters of the state, and was under the NPDES permit system. Officials of this company stated that there was no problem with cyanide in the discharges from the three mills the company operated.
- (4) All but one of the six lead-zinc mills visited in Missouri and the four in Tennessee use cyanide. All but one mill (in Tennessee) use cyanide in almost "starvation" amounts. That one, with extremely high iron sulfide in its feed, used 0.18 lb (0.082 kg/metric ton) of cyanide per ton of ore processed. These Missouri and Tennessee

mills all discharged to waters of the state and operated under the NPDES permit system. Most of the plants practice recycling of mill waters. According to officials, most of the NPDES permits did not limit cyanide, and the measurement for cyanide in effluents was consistently below detectable levels.

- (5) Only two of the plants offered any cost information on their present operation.
- (6) None would hazard an estimate of what the total cost differential might be if a changeover from cyanide to sulfite or sulfide were made.
- (7) On the basis of the information obtained from the company officials contacted, cyanide in effluents did not constitute either an environmental or regulatory problem.

Appendix E presents flowsheets of some of the processes used by the plants visited.

DISCUSSION OF COST OF CONVERTING TO AN ALTERNATIVE REAGENT FOR DEPRESSING PYRITE

During the survey, an attempt was made to obtain information which would provide an insight into the economic impact of converting from cyanide to sulfites or sulfides to depress the flotation of pyrite. It was generally the opinion of all company officials contacted that the actual conversion to alternate depressants in the mill itself probably would not require much plant downtime and probably not much cost differential in reagents. Many thought that such conversion (after justification by properly designed laboratory tests) could be done in a matter of days or a few weeks at most and that within this period they would be able to tell whether or not the alternatives "worked" (i.e., they consistently yielded high recovery and grade over a range of ore feeds). Some indicated that it would take a somewhat longer time to "fine-tune" (i.e., maximize recovery and grade and ascertain that good control was possible) the flotation circuits. One official expressed the opinion that he would not feel comfortable and fully confident of the feasibility of the change until the process modification had operated for a year with consistently satisfactory results.

In Battelle's opinion, based to a large extent on the response of these officials and in consideration of the often complex circuits (particularly in the lead-zinc mills), a reasonably accurate determination of the cost of changeovers cannot be made at this time with the available data.

The components of such a cost include a number of relevant factors, having varying degrees of importance. The differences in the costs of cyanide, sulfite, and sulfide are probably unimportant. The cost of sodium cyanide at the mills visited ranged from 0.5 to 2.5 cents per ton (0.55 to 2.75 cents per metric ton) of ore treated, based on the usage rate the company reported and a unit price of about 50 cents per pound (\$1.10/kg) for sodium

cyanide. One mill, treating an iron-copper-zinc ore to produce iron ore pellets, copper concentrates, and zinc concentrates, reported a usage rate of 0.18 pound per ton (0.082 kg/metric ton) of ore feed, equivalent to about 7 cents per ton (6.35 cents per metric ton). The high usage rate for cyanide at this mill was necessary owing to the high iron content of the feed (about 30 percent Fe as pyrites/pyrrhotite). This mill is not considered to be a typical copper-zinc flotation mill, its major product being iron ore from which copper and zinc would have to be separated in any event. In this mill the separation of copper and zinc by flotation not only removes most of these metals from the iron but produces valuable by-products or co-products.

Considering the cyanide costs (0.5 to 2.5 cents per ton [0.55 to 2.75 cents per metric ton] of ore being processed) characteristic of most of the mills visited which used cyanide, it is difficult to see how converting to sulfide or sulfite could effect any appreciable savings. It is also conjectured that conversion to sulfide or sulfite at these mills might match or would not add significantly to reagent costs. This is a conjecture because little is known at this time about the quantities of sulfide or sulfite which might be required in a given mill to enable the mill to match the metallurgical results now being obtained with cyanide. (One company official stated that his company had tested sulfite as an alternate depressant for pyrite in the laboratory and concluded that it would add significantly to reagent costs because of the greater quantity required.) The quantity of these reagents required is a matter that only can be determined from carefully controlled laboratory tests which simulate mill practice and by confirming tests made in the mill itself.

An additional component of the cost of converting is cost of the laboratory campaign necessary to evaluate the feasibility of converting. Such a campaign could entail a large number of tests to fully evaluate and optimize the conditions required. There is little if any data presently available that could be used to short-cut development work on a given ore, particularly a copper-lead-zinc ore. Some of the data on the use of sulfites or sulfides for pyrite depression in the flotation of copper ore might generally be useful but it would certainly not be adequate to permit optimization of conditions for any given copper ore. However, it is believed that the potential of sulfide and sulfite as depressants for pyrite should be thoroughly explored and not dismissed on the basis of results from a few "pilot" or so-called "critical" tests.

Another component of the cost of converting to sulfides or sulfites as depressants for pyrite might be the cost of adding to or modifying mill equipment to accommodate the process modification. This cost should not be great, but final judgement must be withheld until the results of laboratory development work became available. Whatever increased cost in labor, overhead, and engineering might be incurred in making and completing the change-over in reagents also would be a consideration.

What could be, by far, the greatest cost in any change is the potential reduction in grade and recovery incurred during the start-up of the modified process and possibly even after optimum conditions were determined. Many smelters impose penalties on a case-by-case basis for, say, lower grade concentrates, concentrates with iron and copper percentages above a set

value, etc. due to an equivalent loss of production throughput and greater sulfur oxide capture demand. As an example, one mill reported smelter penalties for off-grade lead concentrates from a mill processing 700 TPD (635 metric tons/day) of ore as follows:

- (1) For every 0.1 percent of copper in excess of 1.0 percent the penalty could amount to \$96,000 per year.
- (2) For every 0.1 percent of iron in excess of 4 percent the penalty could amount to \$264,000 per year.

The penalty is not only imposed on the mills for the other metals in concentrate but also for the increased load on the sulfur oxide capture/utilization facility associated with smelter operations. Due to the presence of the lighter metal sulfides or pyrites, for each ton of lead produced, greater quantities of SO_2 are produced than for higher grade concentrates thereby limiting output of the smelter to its capacity to capture SO_2 .

CONCLUSIONS

The preliminary experimental work included in Phase I suggested that sulfides and sulfites exhibit promise as alternative depressants for pyrite in the flotation treatment of copper, lead, and zinc ores. Work by other investigators cited in the first phase also has indicated that sodium sulfite would be an effective depressant in the flotation of chalcopyrite ores.

The results of this plant survey, however, have shown that the problem is not a simple one. Most of the copper-producing plants visited in the Western United States do not use cyanide to depress pyrite flotation. Virtually all of the lead-zinc producing plants in Missouri and Tennessee use cyanide, but in almost "starvation" amounts. Most of these plants are operated in closed cycle or nearly closed cycle. None admitted to having a cyanide problem related to their effluents.

None of the officials visited in plants using cyanide and discharging to waters of the state knew of or had done any work to determine the mode of occurrence of cyanide in their effluents (i.e., free cyanide, complex cyanides, cyanate, thiocyanate).

The general impression received from these visits was that cyanide in plant discharges does not constitute a significant problem or even a discernable problem in most cases.

It would be unwise, however, to generalize from this impression. Only four states were represented out of about 20 in which copper, lead, and zinc ores are treated for flotation. Only 17 of the estimated 90 to 100 copper-lead-zinc concentrators in the United States were covered. Although the survey failed to disclose any significant problem with cyanide in mill discharges, the possibility that problems do exist in other mills cannot be ruled out.

The following tabulation shows the coverage of the industry provided by the study.

7

State	Approximate Number of Cu-Pb-Zn Mills Listed in Directory*	Number of Mills Visited or Contacted In This Survey
Arizona	21	6
California	1	0
Colorado	9	0
Idaho	7	0
Illinois	5	0
Kentucky	2	0
Maine	1	0
Michigan	1	0
Missouri	7	6
Montana	5	0
Nevada	4	0
New Jersey	1	0
New Mexico	11	0
New York	1	0
Oklahoma	1	0
Tennessee	6	6
Utah	4	3
Virginia	1	0
Washington	1	0
Wisconsin	1	0
Puerto Rico	1	0
TOTAL	91	21

* 1973-74 E/MJ International Director of Mining and Mineral Processing Operations, published by Engineering and Mining Journal, McGraw-Hill, New York, NY, 1974.

RECOMMENDATIONS

It is recommended that the study be continued but that a different approach be adopted--one that would move directly to an objective of eliminating cyanide where this is necessary. The specific steps which should be taken are:

- (1) Query all state or federal regulatory environmental control agencies in states where base-metal milling is practiced, to determine:
 - (a) Which mills operate under NPDES permits;

- (b) Which mills are obliged to meet cyanide limitations in their permits?;
- (c) If a mill uses cyanide, but if its permit does not limit cyanide, why cyanide is not listed?;
- (d) Which mills with cyanide limitations in their permits have violated these limitations within the past 12 months?;
- (e) Of the above, what is the current status and prognosis for future compliance with respect to compliance with cyanide limitations?;
- (f) On what terms does the regulatory agency limit cyanide in these permits (free cyanide, total cyanide, cyanide amenable to chlorination)?;
- (g) Has the regulatory agency itself done any work to determine the mode of occurrence of the cyanide radical in the effluents from the mills under its jurisdiction?;
- (h) Has the mill conducted research studies aimed at substituting other reagents for cyanide?;
- (i) Are reports available on these studies?;
- (j) Has the regulatory agency encouraged any mill with a cyanide problem to seek means to eliminate any cyanide discharge by closing its mill circuit or by installing an end-of-pipe cyanide destruction process?;
- (k) Are reports available on any work covered in (j) above?;
- (l) What is the regulatory agency's assessment of the severity of the cyanide problem caused by base-metal mills under its jurisdiction?

The information requested in Item (l) above would simplify and shorten any program aimed at eliminating cyanide as a mill reagent. It would simplify the programs to define specifically what must be done, and where the trouble spots are.

- (2) The information obtained from the regulatory agencies should be assembled and carefully studied. Should the conclusion be reached that there is no problem with residual cyanide in the effluents from base-metal mills, the project should be abandoned. However, incidents are found at various operations throughout the country where cyanide in effluents has affected the environment.

These cases should be further pursued in this manner:

- (3) Mills with a history of cyanide violations of their NPDES permits and which show no promise of being able to circumvent

their problems, should be approached first. The approach should be deliberate, formal, and ad hoc in nature. The company should be notified that it is expected to seek ways and means to eliminate cyanide from its discharge. It must be recognized that there are several ways to eliminate such discharges. The first is by closing the mill circuit and thus eliminating any cyanide discharge. In regions of the country with abundant rainfall, this could be difficult, though not impossible. A second approach would be to install an end-of-pipe cyanide destruction process. A third option would be to investigate the technical and economic feasibility of substituting sulfides or sulfites for cyanide as depressants for pyrites in the flotation of copper ores and for zinc sulfide and pyrites in the flotation of lead ores. The companies involved should investigate the technical and economic feasibility of these three approaches and should submit reports substantiating their findings. It may be objected that research of the kind required to evaluate the feasibility of using alternative reagents to cyanide ought to be done by outside organizations. This objection is not valid for several reasons. An outside organization would not have sufficient expertise in the company's operation--which is often an art rather than a science. The milling company would be able to test freshly mined ground ore. Any outside organization would be testing ore which is oxidized and not representative of the freshly mined ore being treated. In any event, whatever the "outside" organization found would certainly be contested by the company and would be subject to confirmation by the company's own tests. No "outside" organization knows nearly as much about a company's practices, the ore's variability, or the on-site problems, as the company's metallurgists. The time interval between mining of the ore and the subjection of it to treatment can be critical. Whatever the "outside" organization found, it is sure the company would want to confirm the findings. Whatever work is done on the feasibility of using new reagents must be done by the company. The company would, of course, have to submit a report on its research, which would have to be reviewed and evaluated by "outside" organizations.

- (4) If the results of the studies made by industry, as judged by U.S. EPA or its contractors, indicate that the process can be translated to mill-scale, negotiations should be initiated with the company to make such a transition to demonstrate the procedure.

APPENDIX A

RELEVANT REFERENCES IDENTIFIED BY COMPUTER SEARCH

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BOOKS AND ARTICLES EXAMINED IN THE LITERATURE SEARCH

APPENDIX A

RELEVANT REFERENCES IDENTIFIED BY COMPUTER SEARCH

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APPENDIX B

BASIC INFORMATION EVALUATION AND RANKING OF
DEPRESSANTS UNCOVERED IN THE LITERATURE SEARCH

TABLE B-1. DEPRESSANT: HEAVY METAL SALTS

Basic Information: Performance, Cost, Environmental Hazards, Operating Conditions	Evaluation
Depression of pyrite: AgNO_3, $\text{Hg}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3$, and $\text{Fe}(\text{NO}_3)_3$; all give good pyrite depression (in descending order of effectiveness) at additions of < 7 lb/ton ore. Collector; 0.06 lb/ton KEX; (a) frother: 0.2 lb/ton terpineol (18); (-200 mesh)	<u>Performance</u>: Ag, Cr, and Hg pyrite depression rated as good; Cu, Al, and Fe as poor.
Depression of other sulfide minerals: CR(III) gives good chalcocite depression @ < 0.4 lb/ton. Some metal nitrates, except Ag, give good depression of PbS @ additions < 5 lb/ton (18). Result: not selective for pyrite depression.	<u>Selectivity</u>: Ag selectivity rated as good; Cr, Hg, Cu, Al, and Fe as poor.
<u>Theoretical justification for use</u>: depression may occur through formation of basic metal sulphydryl collector complexes on mineral surfaces (16).	
<u>Environmental hazards</u>: heavy metals would be released in wastewater and tailings disposed of in dumps, ponds, etc.	<u>Environmental considerations</u>: (b) Ag, Cr, Hg, and Cu rated potentially hazardous; Al and Fe rated as less potentially hazardous. Heavy metals in solution are generally considered to be injurious to health and ecological systems above certain concentrations.

(Continued)

TABLE B-1. (Continued)

Basic Information: Performance, Cost, Environmental Hazards, Operating Conditions	Evaluation
<u>Cost information:</u> --	<u>Cost considerations:</u> Ag, Cr, Hg, and Cu salts rated as high cost; Al and Fe as low cost. <u>Development status:</u> None of the metal salts have been subjected to extensive testing as pyrite depressants.

(a) KEX = potassium ethyl xanthate.

(b) See section on Environmental Considerations.

Table B-2. DEPRESSANT: SODIUM SULFIDE (Na_2S)

Basic Information: Performance, Cost, Environmental Hazards, Operating Conditions	Evaluation
Depression of pyrite: 10^{-3} M Na_2S gives excellent depression @ pH 5-6, complete depression @ pH > 10, with KEX(a) collector (7). Reference (19) gives curve of Na_2S concentration versus pH for prevention of contact, using 25 mg/l KEX. One plant gets good results in combination with NaCN, using 0.05 lb/ton ore of Na_2S and 0.013 to 0.015 lb/ton ore of NaCN (20).	<u>Performance:</u> Pyrite depression rated as good.
Depression of other sulfide minerals: Curves given in Reference (19) for PbS, CuFeS_2, FeS_2, and CuS indicate that pyrite is harder to depress with Na_2S than any of the minerals except CuS. Thus, selectivity should be poor except over CuS.	<u>Selectivity:</u> Poor
Theoretical justification for use: References (21) and (18) note that HS^- is the actual depressant when Na_2S is added, since the HS^- concentration is constant along the contact curves. References (7) and (8) claim that S^{2-} is oxidized preferentially to KEX, preventing dioxanthogen formation and pyrite flotation.	<u>Environmental considerations:</u> Potentially nonhazardous unless acidified.
<u>Environmental hazards:</u> If pH goes toward acid side, H_2S could be released to the atmosphere, but this condition is not likely to be encountered in a froth flotation environment.	

(Continued)

TABLE B-2. (Continued)

Basic Information: Performance, Cost, Environmental Hazards, Operating Conditions	Evaluation
<u>Cost information:</u> --	<u>Cost considerations:</u> Low cost per ton of ore processed.
	<u>Development status:</u> Rated as high due to commercial use as depressant.

(a) KEX = potassium ethyl xanthate.

Table B-3. DEPRESSANT: SODIUM THIOSULFATE ($\text{Na}_2\text{S}_2\text{O}_3$)

Basic Information: Performance, Cost, Environmental Hazards, Operating Conditions	Evaluation
<u>Depression of pyrite:</u> Reference (7): Good pyrite depression (>50%) @ pH 6. Reference (22): Using KEX(a) collector, n-amyl alcohol frother, pH = 9.2, 200g KCN/ton, 600g ZnSO_4/ton, 800g NaOH/ton; ore assay: 88.3% <200 mesh, 0.62% Pb, 2.7% Zn, 3.31% FeS_2 sulfur; with 700g/ton-$\text{Na}_2\text{S}_2\text{O}_3$ depressant, 88% of FeS_2 rejected to tails; w/o $\text{Na}_2\text{S}_2\text{O}_3$, 10.5% FeS_2 rejected to tails.	<u>Performance:</u> Good.
<u>Depression of other sulfide minerals:</u> Same ore as above, with $\text{Na}_2\text{S}_2\text{O}_3$: 5.3% of Cu, 16.2% of Pb, 27.6% of Zn rej. to tails; w/o $\text{Na}_2\text{S}_2\text{O}_3$: 5.8% of Cu, 14.9% of Pb, 6.6% of Zn rej. to tails.	<u>Selectivity:</u> Good.
<u>Theoretical justification for use:</u> Reference (7) claims that $\text{Na}_2\text{S}_2\text{O}_3$ reduces solution-oxidation pot., thus preventing xanthate oxidation to dixanthate.	
<u>Environmental hazards:</u> --	<u>Environmental considerations:</u> Non-hazardous.
<u>Cost information:</u> --	<u>Cost considerations:</u> Low cost per ton of ore processed.
	<u>Developmental status:</u> Insufficient information.

(a) KEX = potassium ethyl xanthate.

TABLE B-4. DEPRESSANT: SODIUM HYPOPHOSPHITE ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$)

Basic Information: Performance, Cost, Environmental Hazards, Operating Conditions	Evaluation
Depression of pyrite: 10^{-3} M solution used with KEX(a) collector (2×10^{-4} M) gives 60% depression @ pH -5.5, 90% @ pH -8 (7).	<u>Performance:</u> Good.
<u>Depression of other sulfide minerals:</u>	<u>Selectivity:</u> Insufficient information.
Theoretical justification for use: Reduces solution oxidation potential, preventing oxidation of xanthate (7).	
<u>Environmental hazards:</u> --	<u>Environmental considerations:</u> Insufficient information.
<u>Cost information:</u> --	<u>Cost considerations:</u> Probably high cost per ton of ore processed.
	<u>Developmental status:</u> Not developed beyond screening test stage.

(a) KEX = potassium ethyl xanthate.

TABLE B-5. DEPRESSANT: SODIUM OXALATE ($\text{Na}_2\text{C}_2\text{O}_4$)

Basic Information: Performance, Cost, Environmental Hazards, Operating Conditions	Evaluation
<u>Depression of pyrite:</u> 10^{-3} M solution used with 2×10^{-4} M KEX(a) collector gives 60% depression @ pH -7.5, 90% @ pH -9 (7).	<u>Performance:</u> Good.
<u>Depression of other sulfide minerals:</u>	<u>Selectivity:</u> Insufficient information.
<u>Theoretical justification for use:</u> Reduces solution oxidation potential, stopping xanthate oxidation (18).	
<u>Environmental hazards:</u> --	<u>Environmental considerations:</u> Hazardous.
<u>Cost information:</u>	<u>Cost considerations:</u> Low cost per ton of ore processed.
	<u>Developmental status:</u> Not developed beyond screening test stage.

(a) KEX = potassium ethyl xanthate.

TABLE B-6. DEPRESSANT: SODIUM SULFITE (Na_2SO_3)

Basic Information: Performance, Cost, Environmental Hazards, Operating Conditions	Evaluation
Depression of pyrite: 10^{-3} M Na_2SO_3 gives 80% depression @ pH -6, with 2×10^{-4} M KEX(a) collector, particle size 65 x 100 mesh. Not as good for -200 mesh particles (7).	<u>Performance:</u> Good.
Depression of other sulfide minerals: With same reagent concentrations, doesn't depress PbS until pH > 11. Has been used for ZnS depression in Pb-Zn ores (21).	<u>Selectivity:</u> Good.
Theoretical justification for use: Reduces solution oxidation potential, preventing oxidation of xanthate (7).	
<u>Environmental hazards:</u> --	<u>Environmental considerations:</u> Non-hazardous.
<u>Cost information:</u> --	<u>Cost considerations:</u> Low cost per ton of ore processed.
	<u>Development status:</u> High; used commercially in some cases.

(a) KEX = potassium ethyl xanthate.

TABLE B-7. DEPRESSANT: POTASSIUM PERMANGANATE (KMnO_4)

Basic Information: Performance, Cost, Environmental Hazards, Operating Conditions	Evaluation
<u>Depression of pyrite:</u> Reference (23) says dichromate and permanganate are "two of the most effective depressants" for pyrite; gives no theoretical justification. Reference (18) gives plot of pyrite recovery (%) versus added salt (lb/ton). Addition of 0.4 lb KMnO_4 per ton pyrite gives complete depression using 0.05 lb/ton xanthate and 0.20 lb/ton terpineol frother. 100 x 200 mesh particles, pH unknown. <u>Depression of other sulfide minerals:</u> <u>Theoretical justification for use:</u> <u>Environmental hazards:</u> Mn is a toxic heavy metal. <u>Cost information:</u>	<u>Performance:</u> Good. <u>Selectivity:</u> Insufficient information. <u>Environmental considerations:</u> Hazardous. <u>Cost considerations:</u> High cost per ton of ore processed. <u>Developmental status:</u> Not developed beyond screening test stage.

TABLE B-8. DEPRESSANT: SODIUM DICHROMATE ($\text{Na}_2\text{Cr}_2\text{O}_7$)

Basic Information: Performance, Cost, Environmental Hazards, Operating Conditions	Evaluation
<u>Depression of pyrite:</u> Reference (23) says dichromate and permanganate are "two of the most effective depressants" for pyrite. Reference (18) gives plot of pyrite recovery (%) versus added salt (lb/ton). Addition of 0.2 lb/ton $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ gives 95% pyrite depression [0.3 lb/ton gives complete depression, using 0.05 lb/ton xanthate, and 0.20 lb/ton terpineol frother]; 100 x 200 mesh particle size, pH unknown.	<u>Performance:</u> Good.
<u>Depression of other sulfide minerals:</u> --	<u>Selectivity:</u> Insufficient information.
<u>Theoretical justification for use:</u> --	
<u>Environmental hazards:</u> Cr(VI) is carcinogenic heavy metal.	<u>Environmental considerations:</u> Hazardous.
<u>Cost information:</u>	<u>Cost considerations:</u> High cost per ton of ore processed.
	<u>Developmental status:</u> Not developed beyond screening test stage.

TABLE B-9. DEPRESSANT: Kr6D

Basic Information: Performance, Cost, Environmental Hazards, Operating Conditions	Evaluation
<u>Depression of pyrite: --</u>	<u>Performance:</u> Insufficient information.
Depression of other sulfide minerals: 10 ppm completely depressed ZnS, 5 ppm dep. PbS, 100 ppm CuFeS ₂ and MoS ₂ , using 20 mg/l KAX(a) collector, pH 8.0. With Cu-Pb-Zn ore, obtained best selection of Cu float. using KEX + Z - 200 coll., 0.2 kg/t Na ₂ Cr ₂ O ₇ , 0.05 kg/t Kr6D. Ore assay: 11.8 CuFeS ₂ , 53.5 PbS, 13.5% ZnS; product assay: 41.5 CuFeS ₂ , 26.0 PbS, 25.9% ZnS (24,25).	<u>Selectivity:</u> Good.
<u>Theoretical justification for use:</u> Unknown.	
<u>Environmental hazards:</u> --	<u>Environmental considerations:</u> Insufficient information.
	<u>Cost considerations:</u> Insufficient information.
	<u>Developmental status:</u> Insufficient information.
(a) KAX = potassium amyl xanthate.	

APPENDIX C

TABLE C-1. MILLS VISITED DURING STUDY
(Identified Alphabetically Only)

and

TABLE C-2. FORM USED FOR DISCUSSION WITH
PLANT CONTACT

TABLE C-1. MILLS VISITED DURING STUDY

Date of Visit	Plant	Location	Mill Products	Title
10/29/79	A	Arizona	Cu, Mo, Concentrates	Mill Superintendent
10/30/79	B	Arizona	Cu, Mo, Concentrates	Mill Superintendent
	C	Arizona	Cu, Mo, Concentrates	Mill Superintendent
10/31/79	D	Arizona	Cu Concentrates	Mill Superintendent
11/01/79	E	Utah	Cu, Mo, Concentrates	Mill Superintendent
	F	Utah	Cu, Mo, Concentrates	Mill Superintendent
	G	Utah	Cu, Mo, Concentrates	Mill Superintendent
11/06/79	H	Missouri	Cu, Pb, Zn, Concentrates	Assistant Director Research
	I	Missouri	Cu, Pb, Zn, Concentrates	Assistant Director Research
	J	Missouri	Cu, Pb, Zn, Concentrates	Assistant Director Research
	K	Missouri	Pb, Zn Concentrates	Assistant Director Research
	L	Missouri	Cu, Pb, Zn, Concentrates	Mill Superintendent
	M	Missouri	Pb, Zn, Concentrates	Concentrator Superintendent
11/08/79	N	Tennessee	Cu, Zn, Concentrates	Mill Superintendent
11/09/79	O	Tennessee	Zn Concentrates	Engineer
	P	Tennessee	Zn Concentrates	Engineer
	Q	Tennessee	Zn Concentrates	Engineer

TABLE C-2. FORM USED FOR DISCUSSION WITH
PLANT CONTACT

Company _____ Contact _____ Date _____
Location _____ Title _____ Phone No. _____
Mill Name _____

Production Data

Material	Wt t/day	Grade, %			Recovery, %
		Cu	Pb	Zn	
Feed					
Copper Conc.					
Lead Conc.					
Zinc Conc.					

Cyanide Usage

Point of Addition	Amount Added, lbs/ton	Purpose
_____	_____	_____
_____	_____	_____
_____	_____	_____

Discharge Data

Discharge, gpd _____ CN in discharge, ppm _____ Form of CN in discharge _____
Is there NPDES permit? _____ Does it limit CN? _____ To what level? _____ In compliance? _____
Do you have an end-of-pipe CN destruct system? _____ If so, what process _____

Feasibility of Converting

Familiar with alternate pyrite depressants? _____ Any experience with them? _____
Do you think they work as well as CN? _____ Why? _____
If they could be shown to work in your mill, how long would it take to install the process? _____
Would you be willing to make laboratory tests to verify whether alternates would work? _____
We would appreciate any other comments: _____

APPENDIX D

DATA SHEETS FROM MILLS A THROUGH Q

and

DISCUSSION OF DATA OBTAINED

TABLE D-1. PLANT A

Company _____ Contact _____ Date _____
 Location Arizona Title Mill Superintendent Phone No. _____
 Mill Name _____

Production Data

Material	Wt t/day	Grade, %			Recovery, %
		Cu	Pb	Zn	
Feed	64,000	0.75	-	-	-
Copper Conc.	1300-1500	28	-	-	84
Lead Conc.	-	-	-	-	-
Zinc Conc.	-	-	-	-	-

Cyanide Usage

Point of Addition	Amount Added, lbs/ton	Purpose
None added		

Discharge Data

Discharge, gpd None CN in discharge, ppm NA Form of CN in discharge NA
 Is there NPDES permit? No Does it limit CN? NA To what level? NA In compliance? NA
 Do you have an end-of-pipe CN destruct system? No If so, what process NA

Feasibility of Converting

Familiar with alternate pyrite depressants? Yes Any experience with them? _____
 Do you think they work as well as CN? Maybe Why? _____
 If they could be shown to work in your mill, how long would it take to install the process? Matter of days
 Would you be willing to make laboratory tests to verify whether alternates would work? Don't require
 We would appreciate any other comments: Have used Na₂SO₃ in a heavily limed circuit at another mill to reduce viscosity and increase throughput in grinding circuit. Milling and flotation process used at _____ has been described in a paper presented at the Gaudin Flotation Symposium, held in Las Vegas, in 1976.

TABLE D-2. PLANT B

Company _____ Contact _____ Date 10/30/79
 Location Arizona Title Mill Superintendent Phone No. _____
 Mill Name _____

Production Data

Material	Wt t/day	Grade, %			Recovery, %
		Cu	Pb	Zn	
Feed	92,000	0.25	-	-	-
Copper Conc.	1,250	25	-	-	90+
Lead Conc.	-	-	-	-	-
Zinc Conc.	-	-	-	-	-
Other	Mo, Ag				

Cyanide Usage

Point of Addition	Amount Added, lbs/ton	Purpose
<u>No cyanide used</u>	<u>NA</u>	<u>NA</u>
_____	_____	_____
_____	_____	_____

Discharge Data

Discharge, gpd None CN in discharge, ppm NA Form of CN in discharge NA
 Is there NPDES permit? No Does it limit CN? NA To what level? NA In compliance? NA
 Do you have an end-of-pipe CN destruct system? No If so, what process NA

Feasibility of Converting

Familiar with alternate pyrite depressants? Yes Any experience with them? No
 Do you think they work as well as CN? No opinion Why? NA
 If they could be shown to work in your mill, how long would it take to install the process? About 1 month
 Would you be willing to make laboratory tests to verify whether alternates would work? No need
 We would appreciate any other comments: _____

TABLE D-3. PLANT C

Company _____ Contact _____ Date _____
 Location Arizona Title Mill Superintendent Phone No. _____
 Mill Name _____

Production Data

Material	Wt t/day	Grade, %			Recovery, %
		Cu	Pb	Zn	
Feed	50,000*	0.5	-	-	-
Copper Conc.	-	-	-	-	Ca 90
Lead Conc.	-	-	-	-	-
Zinc Conc.	-	-	-	-	-

Cyanide Usage

Point of Addition	Amount Added, lbs/ton	Purpose
<u>None now used</u>	<u>NA</u>	<u>NA</u>
_____	_____	_____
_____	_____	_____

Discharge Data

Discharge, gpd Sanitary only CN in discharge, ppm None Form of CN in discharge NA
 Is there NPDES permit? No Does it limit CN? NA To what level? NA In compliance? NA
 Do you have an end-of-pipe CN destruct system? No If so, what process NA

Feasibility of Converting

Familiar with alternate pyrite depressants? Yes Any experience with them? Other mills only
 Do you think they work as well as CN? Doubt it Why? _____
 If they could be shown to work in your mill, how long would it take to install the process? No comment
 Would you be willing to make laboratory tests to verify whether alternates would work? No need now
 We would appreciate any other comments: This mill has used cyanide to depress pyrite flotation. Doesn't need it now. If iron in feed got too high, might go back to some cyanide.
 Comment by Battelle: This plant is in the throes of startup. The mill superintendent was extremely busy and couldn't provide much time. We checked with the Arizona EPA. The plant has no record of CN violations. There was a complaint by a rancher but this was concerned with the discharge of the company's sanitary waste to a small stream.

* When in full production.

TABLE D-4. PLANT D

Company _____ Contact _____ Date 10/31/79
 Location Arizona Title Mill Superintendent Phone No. _____
 Mill Name _____

Production Data

Material	Wt t/day	Grade, %			Recovery, %
		Cu	Pb	Zn	
Feed	42,000	0.9	-	-	-
Copper Conc.	1,000	27	-	-	-
Lead Conc.	-	-	-	-	-
Zinc Conc.	-	-	-	-	-

Cyanide Usage

Point of Addition	Amount Added, lbs/ton	Purpose
<u>No cyanide used</u>	<u>NA</u>	<u>NA</u>
_____	_____	_____
_____	_____	_____

Discharge Data

Discharge, gpd No discharge CN in discharge, ppm NA Form of CN in discharge NA
 Is there NPDES permit? No Does it limit CN? NA To what level? NA In compliance? NA
 Do you have an end-of-pipe CN destruct system? No If so, what process NA

Feasibility of Converting

Familiar with alternate pyrite depressants? Yes Any experience with them? In past with NaHS
 Do you think they work as well as CN? No opinion Why? NA
 If they could be shown to work in your mill, how long would it take to install the process? About 1 day
 Would you be willing to make laboratory tests to verify whether alternates would work? If necessary
 We would appreciate any other comments: Mill has four lines. Could assess any reagent changes quickly. Contact gave estimate that flotation costs at Twin Buttes are between 40 and 50 cents per ton.

TABLE D-5. PLANTS E, F, & G

Company _____ Contact _____ Date 11/1/79
 Location Utah Title Mill Superintendent Phone No. _____
 Mill Name _____

Production Data

Material	Wt t/day	Grade, %			Recovery, %
		Cu	Pb	Zn	
Feed	106,000	0.6	-	-	-
Copper Conc.	2,200	25	-	-	88
Lead Conc.	-	-	-	-	-
Zinc Conc.	-	-	-	-	-
Other	Mo, Re, Au, Ag, Pt, Se	-	-	-	-

Cyanide Usage

Point of Addition	Amount Added, lbs/ton	Purpose
_____	_____	_____
_____	_____	_____
_____	_____	_____

Discharge Data

Discharge, gpd Ca 23,000,000^{total} CN in discharge, ppm _____ Form of CN in discharge UK
 Is there NPDES permit? Yes Does it limit CN? Yes To what level? < 0.02ppm In compliance? _____
 Do you have an end-of-pipe CN destruct system? No If so, what process Calspan tried alkaline
chlorination and ozonation in lab.

Feasibility of Converting

Familiar with alternate pyrite depressants? Yes Any experience with them? Not here
 Do you think they work as well as CN? _____ Why? _____
 If they could be shown to work in your mill, how long would it take to install the process? _____
 Would you be willing to make laboratory tests to verify whether alternates would work? _____
 We would appreciate any other comments: Three mills treat the same type of ore from the same
mine. All use the same process and supervised all three.

This plant was studied by Calspan who prepared the Development Document for Metal Mining and Milling Industry.

TABLE D-6. PLANT H

Company _____ Contact _____ Date 11/6/79
 Location Missouri Title Assistant Director of Phone No. _____
 Mill Name _____ Research

Production Data

Material	Wt t/day	Grade, %				Recovery, %
		Cu	Pb	Zn	Fe	
Feed	5000	0.25	5	0.8	Ca 1	-
Copper Conc.	-	-	-	-	-	-
Lead Conc.	400	-	72-74 ¹	-	-	96 ¹
Zinc Conc.	? ²	-	-	52 ¹	-	70 ¹

Cyanide Usage

Point of Addition	Amount Added, lbs/ton	Purpose
Grind, lead & zinc cleaner circuits. Sometimes not added when metallurgy is favorable.	0 to 0.05 lbs per ton of feed	Pyrite depression

Discharge Data

Discharge, gpd Essen. closed CN in discharge, ppm <0.02 Form of CN in discharge Not known
 Is there NPDES permit? Yes Does it limit CN? No To what level? NA In compliance? NA
 Do you have an end-of-pipe CN destruct system? No If so, what process NA

Feasibility of Converting

Familiar with alternate pyrite depressants? Yes Any experience with them? Some. Sulfites also depress Pb and led
 Do you think they work as well as CN? No Why? Perhaps not enough work on them
 If they could be shown to work in your mill, how long would it take to install the process? Depends on how much
 Would you be willing to make laboratory tests to verify whether alternates would work? Yes iron. Matter of days
 We would appreciate any other comments: These apply to other 3 plants also. If CN were ruled out we would of course try others. So far there has been no encouragement to do so. Do not think that CN is a significant problem. Two streams in area are monitored monthly for cyanide. All results <0.02 ppm. No fish kills in area streams for 10 years. Tailing ponds max. 0.05.

- 1) Grades and recoveries shown were given as typical for all four plants owned by the company.
- 2) Weights of zinc concentrates were not cited because they are so variable. Copper concentrates not cited. Company estimated copper concentrates from all four plants to be 12,000 t/yr.

TABLE D-7. PLANT I

Company _____ Contact _____ Date 11/6/79
 Location Missouri Title Assistant Director of Phone No. _____
 Mill Name _____ Research

Production Data

Material	Wt t/day	Grade, %			Recovery, %
		Cu	Pb	Zn	
Feed	7,500	0.25	4	1	-
Copper Conc.	-	-	-	-	-
Lead Conc.	500	-	72-74	-	96+
Zinc Conc.	Variable	0.5	0.8	58	83

Cyanide Usage

Point of Addition	Amount Added, lbs/ton	Purpose
<u>Sometimes to grind</u>	<u>0 to 0.05 lb/ton</u>	<u>Depress pyrite</u>
<u>and cleaner circuits</u>	_____	_____
_____	_____	_____

Discharge Data

closed cycle
 Discharge, gpd Essentially CN in discharge, ppm <0.02 ppm Form of CN in discharge Not known
 Is there NPDES permit? Yes Does it limit CN? No To what level? NA In compliance? NA
 Do you have an end-of-pipe CN destruct system? No If so, what process NA

Feasibility of Converting

Familiar with alternate pyrite depressants? Yes Any experience with them? See Plant H comments
 Do you think they work as well as CN? NA Why? NA
 If they could be shown to work in your mill, how long would it take to install the process? _____
 Would you be willing to make laboratory tests to verify whether alternates would work? _____
 We would appreciate any other comments: See Plant H comments

TABLE D-8. PLANT J

Company _____ Contact _____ Date 11/6/79
 Location Missouri Title Assistant Director of Phone No. _____
 Mill Name _____ Research

Production Data

Material	Wt t/day	Grade, %			Recovery, %
		Cu	Pb	Zn	
Feed	5,000	0.25	8	0.8	-
Copper Conc.	-	-	-	-	-
Lead Conc.	400	-	74	-	98
Zinc Conc.	Variable	-	-	53	60

Cyanide Usage

Point of Addition	Amount Added, lbs/ton	Purpose
<u>Grind Pb and Zn</u>	<u>0 to 0.05 lb/ton</u>	<u>Depress pyrite</u>
<u>cleaners</u>	_____	_____
_____	_____	_____

Discharge Data

closed cycle
 Discharge, gpd Essentially CN in discharge, ppm <0.02 ppm Form of CN in discharge OK
 Is there NPDES permit? Yes Does it limit CN? No To what level? _____ In compliance? _____
 Do you have an end-of-pipe CN destruct system? No If so, what process _____

Feasibility of Converting (See Plant H)

Familiar with alternate pyrite depressants? _____ Any experience with them? _____
 Do you think they work as well as CN? _____ Why? _____
 If they could be shown to work in your mill, how long would it take to install the process? _____
 Would you be willing to make laboratory tests to verify whether alternates would work? _____
 We would appreciate any other comments: _____

TABLE D-9. PLANT K

Company _____ Contact _____ Date 11-6-79
 Location Missouri Title Assistant Director of Phone No. _____
 Mill Name _____ Research

Production Data

Material	Wt t/day	Grade, %			Recovery, %
		Cu	Pb	Zn	
Feed	2,500	0.25	2.5	<0.1	-
Copper Conc.	-	-	-	-	-
Lead Conc.	100	-	72-74	-	-
Zinc Conc.	-	-	-	-	-

Cyanide Usage

Point of Addition	Amount Added, lbs/ton	Purpose
<u>Grind or Pb</u>	<u>0 to 0.05 lb/ton</u>	<u>Depress pyrite</u>
<u>cleaners</u>	_____	_____
_____	_____	_____

Discharge Data

Discharge, gpd Essen. closed cycle CN in discharge, ppm <0.02 Form of CN in discharge _____
 Is there NPDES permit? Yes Does it limit CN? No To what level? _____ In compliance? _____
 Do you have an end-of-pipe CN destruct system? No If so, what process _____

Feasibility of Converting (See Plant H)

Familiar with alternate pyrite depressants? _____ Any experience with them? _____
 Do you think they work as well as CN? _____ Why? _____
 If they could be shown to work in your mill, how long would it take to install the process? _____
 Would you be willing to make laboratory tests to verify whether alternates would work? _____
 We would appreciate any other comments: _____

TABLE D-10. PLANT L

Company _____ Contact _____ Date 11/6/79
 Location Missouri Title Mill Superintendent Phone No. _____
 Mill Name _____

Production Data

Material	Wt t/day	Grade, %				Recovery, %
		Cu	Pb	Zn	Fe	
Feed	4,200	0.3	7	1	3	-
Copper Conc.	32	2.9	1	0.8	1.5	70
Lead Conc.	480	0.4	75	1	1.5	98
Zinc Conc.	64	0.3	1.5-2	62	-	75-80

Cyanide Usage

Point of Addition	Amount Added, lbs/ton	Purpose
<u>Rod mill feed</u>	<u>0.015 to 0.02 lbs/ton</u>	<u>Depress Fe and Zn</u>
<u>Zinc cleaner</u>	_____	_____
_____	_____	_____

Discharge Data

Discharge, gpd Essen. closed cycle CN in discharge, ppm Not detect. Form of CN in discharge _____
 Is there NPDES permit? Yes Does it limit CN? No To what level? _____ In compliance? _____
 Do you have an end-of-pipe CN destruct system? No If so, what process _____

Feasibility of Converting

Familiar with alternate pyrite depressants? Yes Any experience with them? Yes in lab
 Do you think they work as well as CN? No Why? _____
 If they could be shown to work in your mill, how long would it take to install the process? About a week
 Would you be willing to make laboratory tests to verify whether alternates would work? Might
 We would appreciate any other comments: Plant is highly automated with 10 product streams being monitored every 3 minutes via X-ray fluorescence. Cited NaCN at 48¢/lb. Based on data they obtained reagent cost of sulfate would be 8 times that of cyanide to do the same job.

TABLE D-11. PLANT M

Company _____ Contact _____ Date 11/6/79
 Location Missouri Title Contractor Superintendent Phone No. _____
 Mill Name _____

Production Data

Material	Wt t/day	Grade, %				Recovery, %
		Cu	Pb	Zn	Fe	
Feed	6,500	0.2	8	2.5	2.5	-
Copper Conc.	-	-	-	-	-	-
Lead Conc.	600	-	75	1.2	-	-
Zinc Conc.	250	-	1.4	58	-	-

Cyanide Usage

Point of Addition	Amount Added, lbs/ton	Purpose
<u>Lead cleaner</u>	<u>0.01 lb/ton</u>	<u>Depress pyrite</u>
_____	_____	_____
_____	_____	_____

Discharge Data

Discharge, gpd 3500 CN in discharge, ppm <0.02 Form of CN in discharge _____
 Is there NPDES permit? Yes Does it limit CN? Yes To what level? 0.02 In compliance? *
 Do you have an end-of-pipe CN destruct system? _____ If so, what process _____

Feasibility of Converting

Familiar with alternate pyrite depressants? Yes Any experience with them? Limited
 Do you think they work as well as CN? Doubt Why? _____
 If they could be shown to work in your mill, how long would it take to install the process? A year to convince
 Would you be willing to make laboratory tests to verify whether alternates would work? _____ him
 We would appreciate any other comments: _____

* In winter may exceed rarely.

TABLE D-12. PLANT N

Company _____ Contact _____ Date 11/8/79
 Location Tennessee Title Mgr., Eng. Indus. Chem. Op. Phone No. _____
 Mill Name _____

Production Data

Material	Wt t/day	Grade, %				Recovery, %
		Cu	Pb	Zn	Fe	
Feed	7,000	0.72	-	0.6	31.5	-
Copper Conc.	210	17	-	-	-	75
Lead Conc.	-	-	-	-	-	-
Zinc Conc.	25	-	-	48-50	-	30-32
Iron	3,100	-	-	-	55-56	80

Cyanide Usage

Point of Addition	Amount Added, lbs/ton	Purpose
Copper rougher	0.1 lb/ton	Depress Fe
Smaller amount to		and Zn
Cu cleaner	0.06 to 0.08 lb/ton	

Discharge Data

Discharge, gpd 6,000 CN in discharge, ppm _____ Form of CN in discharge OK
 Is there NPDES permit? Yes Does it limit CN? Yes To what level? 0.5 kg/day In compliance? _____
 Do you have an end-of-pipe CN destruct system? No If so, what process loading

Feasibility of Converting

Familiar with alternate pyrite depressants? Yes, sulfites Any experience with them? Yes, several yrs. ago
 Do you think they work as well as CN? No Why? Based on results
 If they could be shown to work in your mill, how long would it take to install the process? 2 or 3 days
 Would you be willing to make laboratory tests to verify whether alternates would work? _____
 We would appreciate any other comments: _____

TABLE D-13. PLANT O

Company _____ Contact _____ Date 11/9/79
 Location Tennessee Title Engineer Phone No. _____
 Mill Name _____

Production Data

Material	Wt t/day	Grade, %			Recovery, %
		Cu	Pb	Zn	
Feed	6,500	-	-	2.5	-
Copper Conc.	-	-	-	-	-
Lead Conc.	-	-	-	-	-
Zinc Conc.	250	-	-	62.5	Ca 97-98

Cyanide Usage

Point of Addition	Amount Added, lbs/ton	Purpose
<u>Ball mill feed</u>	<u>0.02 lbs/ton</u>	<u>Depress iron</u>
<u>and to roughers</u>	<u>when needed</u>	_____
<u>and cleaners</u>	_____	_____

Discharge Data

Discharge, gpd Closed cycle CN in discharge, ppm _____ Form of CN in discharge _____
 Is there NPDES permit? Yes Does it limit CN? No To what level? _____ In compliance? _____
 Do you have an end-of-pipe CN destruct system? No If so, what process _____

Feasibility of Converting

Familiar with alternate pyrite depressants? _____ Any experience with them? _____
 Do you think they work as well as CN? _____ Why? _____
 If they could be shown to work in your mill, how long would it take to install the process? _____
 Would you be willing to make laboratory tests to verify whether alternates would work? _____
 We would appreciate any other comments: Formerly used lime as depressant. By using starvation
quantities of cyanide have been able to cut iron in concentrates from about 3.0 to 0.5 percent.

TABLE D-14. PLANT P

Company _____ Contact _____ Date 11/9/79
 Location Tennessee Title Engineer Phone No. _____
 Mill Name _____

Production Data

Material	Wt t/day	Grade, %			Recovery, %
		Cu	Pb	Zn	
Feed	3,200	-	-	2.5	-
Copper Conc.	-	-	-	-	-
Lead Conc.	-	-	-	-	-
Zinc Conc.	Ca 120	-	-	63	96

Cyanide Usage

Point of Addition	Amount Added, lbs/ton	Purpose
<u>Ball mill feed</u>	<u>0.02 lb/ton when</u>	<u>Depress iron</u>
<u>and roughers</u>	<u>needed</u>	
<u>and cleaners</u>		

Discharge Data (See Plant 0)

Discharge, gpd _____ CN in discharge, ppm _____ Form of CN in discharge _____
 Is there NPDES permit? _____ Does it limit CN? _____ To what level? _____ In compliance? _____
 Do you have an end-of-pipe CN destruct system? _____ If so, what process _____

Feasibility of Converting (See Plant 0)

Familiar with alternate pyrite depressants? _____ Any experience with them? _____
 Do you think they work as well as CN? _____ Why? _____
 If they could be shown to work in your mill, how long would it take to install the process? _____
 Would you be willing to make laboratory tests to verify whether alternates would work? _____
 We would appreciate any other comments: _____

TABLE D-15. PLANT Q

Company _____ Contact _____ Date 11/9/79
 Location Tennessee Title Engineer Phone No. _____
 Mill Name _____

Production Data

Material	Wt t/day	Grade, %				Recovery, %
		Cu	Pb	Zn	Fe	
Feed	1,900	-	-	2.5	263	-
Copper Conc.	-	-	-	-	-	-
Lead Conc.	-	-	-	-	-	-
Zinc Conc.	75	-	-	58-59	-	92

Cyanide Usage

Point of Addition	Amount Added, lbs/ton	Purpose
<u>Cleaner</u>	<u>0.02 lb/ton</u>	<u>Depress Fe</u>
_____	_____	_____
_____	_____	_____

Discharge Data

Discharge, gpd _____ CN in discharge, ppm <.02 Form of CN in discharge OK
 Is there NPDES permit? Yes Does it limit CN? No To what level? _____ In compliance? _____
 Do you have an end-of-pipe CN destruct system? No If so, what process _____

Feasibility of Converting

Familiar with alternate pyrite depressants? Yes, Na₂SO₃ Any experience with them? 26 mo. lab experience
 Do you think they work as well as CN? No Why? Based on our results
 If they could be shown to work in your mill, how long would it take to install the process? Several days
 Would you be willing to make laboratory tests to verify whether alternates would work? _____
 We would appreciate any other comments: Company is going to close the circuit on this mill.
Experience at other mills in the area has shown this can be done with no adverse effects from buildup of reagents.

APPENDIX D

DISCUSSION OF DATA OBTAINED

WESTERN MILLS

Four plants in southern Arizona and three in Utah were visited. All were predominantly copper producers. The information they furnished is summarized and then treated individually as Plants A through G.

Plant A (Table D-1)

This is primarily a copper mill treating over 60,000 tons (54,400 metric tons) per day of ore containing about 0.75 percent copper, and producing over 1,000 tons (900 metric tons) per day of copper concentrates at a grade of about 30 percent copper and a recovery of about 85 percent. It also produces a by-product, molybdenum sulfide. Gold and silver are recovered from copper concentrates after smelting and refining.

This company uses no cyanide to depress pyrite in the copper flotation section, but does use a small amount of cyanide to depress copper in the recovery of molybdenum sulfide from the final cleaned molybdenum concentrate.

The company has no discharge to waters of the state from the mill, returning all excess water from tailings ponds and thickeners to the mill for reuse. Consequently, no NPDES permit is required for the mill operation. Battelle did not determine whether the company smelter or refinery discharged to state waters.

The mill superintendent was aware that sodium sulfite and sodium sulfide, or related chemicals, could be used to depress pyrite, but had no direct experience with these for this purpose.

No flow diagram of the mill operation was on hand, but an excellent brochure describing the operation of the mining, milling, smelting and refining was provided for perusal.

Plant B (Table D-2)

This, too, is a large copper mill in southern Arizona, producing mainly copper, with molybdenum and silver by-products. The feed containing only about 0.35 percent copper amounts to about 90,000 tons (81,650 metric tons) per day. The mill produces from this about 1,300 tons (1,180 metric tons) of copper concentrates assaying about 25 percent copper. Recovery is over 90 percent.

As is the case with Plant A, this mill does not use cyanide in its flotation circuit for pyrite depression, has no discharge, and does not have or need an NPDES permit.

The company spokesman estimated that if the mill were using cyanide, and wished to substitute sulfide or sulfite for it, and was able to substantiate the efficacy of the substitutes by thorough and definitive testing, the

changeover in the production mill might be accomplished in about 3 weeks to 1 month.

Plant C (Table D-3)

This plant had been out of production for some time and was only now approaching about half its capacity. The mill superintendent was extremely busy and was able to grant only a relatively brief interview. Principal products are copper, molybdenum, and silver. Mill feed, at normal capacity, was about 50,000 tons (45,360 metric tons) per day with the feed running about 0.5 percent copper. Although the mill had used cyanide in the past as a pyrite depressant, it had discontinued the practice. According to the superintendent, it might be necessary in the future to go back to cyanide if problems should arise from the presence of increasing quantities of pyrite in the concentrate. He was familiar with the properties of sulfite and sulfide as depressants but had no direct experience with them. The company has no process wastewater discharge and no NPDES permit.

Plant D (Table D-4)

This plant operates primarily as a copper concentrator, treating 42,000 tons/day (36,290 metric tons/day) of ore running about 0.9 percent copper. It produces about 1,000 tons/day (907 metric tons/day) of copper concentrates at a grade of about 27 percent copper. Recoveries are in the range of 87 to 93 percent, according to the superintendent. This is considerably higher than the recovery figure calculated from the weights and grades of feed and concentrates, and it is suspected that the numbers given during the interview had been rounded off. This plant does not use cyanide as pyrite depressant, has no discharge and no NPDES permit. The superintendent stated that if it became expedient to change a flotation reagent and if laboratory tests indicated the technical and economic feasibility of doing so, it would only require about one day's mill operation to change over.

Plants E, F, and G (Table D-5)

These three mills treat the output of one mine. Feed to the mills amounts to over 100,000 tons/day (90,720 metric tons/day) and has an average copper content of 0.6 percent. The mills produce together over 2,000 tons/day (1,800 metric tons/day) of concentrate at an average grade of 25 percent copper. Recovery is about 90 percent. In addition to copper, operations belonging to the company recover molybdenum, gold, silver, selenium, platinum, palladium, and various rhenium salts.

These mills use sodium cyanide to depress pyrite during copper flotation at a feed rate of 0.02 lb/ton (0.0091 kg/metric ton) of ore.

The company discharges to waters of the state from its mills and operates under an NPDES permit. The total cyanide limitation set by the permit is 0.006 ppm. The superintendent stated that they have had no problem with the U.S. EPA in the matter of cyanide violations. The company has an end-of-pipe wastewater treatment system, but this is primarily to control oil, metals, and suspended solids and does not include a cyanide destruction unit.

These plants were studied by the contractor for U.S. EPA who prepared the Development Document for the Metal Mining Industry Point Source Category.

Other Arizona Contacts

To determine whether the plants visited were typical of copper milling in this part of the country, a call was made to the head offices of a major mining company in the region, which operates three copper mines and mills treating about 50,000 tons/day (45,360 metric tons/day). As with the plants visited, none of this company's mills used cyanide to depress pyrite in their copper flotation circuits.

MISSOURI MILLS

Three companies controlling six mills were interviewed in Missouri. All these were primarily lead and zinc producers with copper being a relatively minor by-product. They are discussed individually under the designation of Plants H through M.

Plants H, I, J, and K (Tables D-6 through D-9)

These four mills treat from 1,200 to 7,500 tons/day (1,090 to 6,800 metric tons/day) of ore from the parent company's mines. Ore grades are variable. The ranges of ore composition are as follows:

- Pb - 2.5 to 8 percent
- Zn - 0.1 to 0.8 percent
- Cu - about 0.25 percent in all cases
- Fe - 1 to 3 percent.

The weight of concentrates produced is also variable, depending on the feed tonnage, ore grade, etc., at the individual mills, ore characteristics, and response to reagents. Lead concentrate tonnage ranges from 100 to 700 tons/day (91 to 635 metric tons/day) at a fairly consistent grade of over 70 percent lead. Zinc concentrate tonnages, according to the company representative, vary "all over the lot" at a grade of about 50 to 52 percent zinc. All four mills together produce about 15,000 tons (13,600 metric tons) of copper concentrates. Overall recoveries cited were as follows:

- Pb = 96 percent
- Zn = 70 percent
- Cu = 70 percent.

Sodium cyanide is used to depress pyrite. Cyanide additions range from 0 to .005 lb/ton (0 to 0.0023 kg/metric ton) and are made either in the grinding step, or in the cleaning steps. On some occasions, depending on the metallurgy, no cyanide additions at all are made at two of the four mills. The company representative indicated that at the two other mills, with higher iron assays, cyanide was always added and that he would hesitate to predict the effect of not adding cyanide on the grade and composition of the lead and zinc concentrates. He also stated that if cyanide were ever ruled out for use

in the mills the company would be forced to take other steps, look at other alternatives. Up to now, he said, they had received no impetus or encouragement to look at other alternatives.

At all four plants, recycling of water is maximized and, except after heavy rains, the systems are essentially closed cycle with any makeup being supplied by mine water. Discharges do occur, however, and each mill operates under a separate NPDES permit.

Effluents from the plants consistently contain 0.02 ppm cyanide as determined colorimetrically. Distillation is not used in the analysis. There is a probability therefore that complex cyanides (e.g., as iron hexacyano complex ion) may be present in mill effluents.

Five streams in the area of the plants are analyzed monthly for cyanide. No detectable cyanide has been found in these stream samples. According to the company's environmental supervisor, there have been no fish kills in these streams for at least 10 years.

The company's assistant director of research stated that even if laboratory tests indicated that sulfide or sulfite could be used to supplant cyanide as a depressant for iron, its adoption would depend on the iron concentration ratio in the mill feed, and he pointed out that in two of the four mills iron concentrations were unpredictably variable. If proper and decisive laboratory tests did indicate the feasibility of substituting either sulfide or sulfite for cyanide, and if the changeover were made, he expected that the response in the production circuit could be judged, but he would not speculate on the time it would take for the changeover to reach steady state.

Plant L (Table D-10)

This plant produces copper, lead, and zinc concentrates. It treats 4,200 tons/day (3,810 metric tons/day) of an ore containing about 7 percent lead, 1 percent zinc, 0.3 percent copper, and 3 percent iron. The plant operates on a five-day/week basis on about 250 days per year.

Average daily production of concentrates is as follows:

Pb	=	480 tons (435 metric tons)
Zn	=	64 tons (58 metric tons)
Cu	=	32 tons (29 metric tons).

Concentrate grades and recoveries are shown in the following tabulation:

Concentrate Grades, %					
Concentrates	Pb	Zn	Cu	Fe	Recovery, %
Pb	75	1	0.4	1.5	97.5
Zn	1.5-2.0	61.5	0.5	1.5	75-80
Cu	4	0.8	29	28	70

Cyanide to depress both iron and zinc is added in the rod mill and the zinc cleaner. Cyanide additions range from 0.015 to 0.02 lb/ton (0.0075 to .010 kg/metric ton) of feed.

The company discharges to waters of the state and so must operate under an NPDES permit. The original NPDES permit had set cyanide restrictions at a level below detectable limits. The present permit does not limit cyanide. Cyanide is presently not detectable in the effluent from the plant. This is attributed to the small amounts of cyanide used and to the continuous analysis and computerized control system employed. A company official estimated that it would take about one week of mill operation to determine the effect of the change due to the reagent substitution.

This company had tested sulfite as a depressant and stated that it had worked in the laboratory tests. The quantity of sulfite required, however, was quite high. The interviewed official stated that where annual cyanide costs were \$7,000 to \$8,000, sulfite costs would exceed \$63,000. Documentation of these results was not provided to Battelle's Columbus Laboratories.

Plant M (Table D-11)

The plant produces lead and zinc concentrates only. It treats 6,500 tons/day (5,900 metric tons/day) of ore with an average grade of about 8 percent lead, 2.5 percent zinc, 0.2 percent copper, and 2.5 percent iron. It produces 600 tons/day (544 metric tons/day) of lead concentrates containing about 75 percent lead and 1.2 percent zinc. It also produces about 250 tons/day (227 metric tons/day) of zinc concentrates containing 58 percent zinc and 1.4 percent lead. Calculated recoveries, based on these data, are lead - 85 to 90 percent, and zinc - about 90 percent.

Cyanide is added to the lead cleaner circuit at a rate of about 0.01 lb/ton (0.0045 kg/metric ton) of ore to depress pyrite during flotation.

The company discharges wastewater at a rate of 3,500 gpm (13,250 liters/min). Its NPDES permit limits cyanide to 0.02 ppm. This limitation was exceeded only once in the past several years and only during the winter.

The company spokesman stated that it would take a year of good mill operation to convince him that the reagent changeover substituting sulfides or sulfites for cyanide was acceptable.

TENNESSEE MILLS

Three companies controlling four mills were interviewed in Tennessee. Three of these mills were zinc concentrate producers and the fourth was primarily an iron oxide producer with copper and zinc as coproducts. These mills are designated as Plants N, O, P, and Q.

Plant N (Table D-12)

This plant produces zinc and copper concentrates, as well as iron sulfide concentrates which are later roasted to oxide and eventually sold for iron ore. The mill treats 7,000 tons/day (6,350 metric tons/day) of ore containing about 0.6 percent zinc, 0.72 percent copper, and about 32 percent iron. The iron in the ore occurs as pyrrhotite and pyrite in a ratio of 4:1, respectively. Its daily production is about 210 tons/day (190 metric tons/day) of copper concentrates containing from 15 to 20 percent copper, and 25 tons/day (23 metric tons/day) of zinc concentrates containing about 50 percent zinc. Approximate recoveries for copper and zinc are about 75 and 30 to 35 percent, respectively.

The company employs sodium cyanide to depress both iron and zinc adding about 0.1 lb/ton (0.045 kg/metric ton) to the copper rougher circuit and an additional 0.06 to 0.08 lb/ton (0.027 to 0.036 kg/metric ton) to the copper cleaner circuit. The relatively high rate of cyanide addition is necessary because of the high iron content of the ore.

The entire plant discharges about 6,000 gpm (22,712 liters/min) of wastewater to surface streams and operates under an NPDES permit. The permit limits the discharge of cyanide to 0.5 kg average and 0.7 kg maximum, per day. On the basis of the data provided, these loadings calculate out to concentrations of about 0.015 ppm average and about 0.02 ppm maximum. These limits are not consistent.

The company had investigated sulfites or bisulfites as depressants some years ago, and the spokesman stated that the program did not "work out too well". It was stated that it would be difficult to simulate their copper circuit in laboratory tests. It was estimated that if the mill circuit were changed from cyanide to sulfite or sulfide for iron depression, it would only take 2 or 3 days to evaluate the workability of the change but that it probably would take several months to fine-tune the system (i.e., maximize the grade of the isolated fractions).

Plants O and P (Tables D-13 and D-14)

Both of these plants are temporarily shut down and are undergoing some revision in equipment. Plant O, when operating, treats 6,200 to 6,500 tons (5,625 to 5,900 metric tons) of ore per day containing 2.5 percent zinc. It produces about 250 tons/day (227 metric tons/day) of zinc concentrates at a grade of 62.5 percent zinc at a recovery of 97 to 98 percent. This mill employs heavy media separation prior to flotation, and the feed to flotation is thereby upgraded to about 5 percent zinc.

Cyanide addition, amounting to about 0.02 lb/ton (0.0091 kg/metric ton) of original feed, is made to ball mill feed or to the zinc rougher or cleaner circuits, when needed, which is only part of the time.

The mill is operated in complete closed circuit and, according to officials, there is no cyanide discharge. Recycling does not result in a buildup of collectors in the circuit. Frothers do build up, but this is regarded as an advantage.

Plant P treats, when operating, 3,200 tons/day (2,900 metric tons/day) of ore containing 2.5 percent zinc, and produces about 120 tons/day (109 metric tons/day) of zinc concentrate containing about 63 percent zinc at a recovery of 96 percent.

No cyanide is used in this mill.

Plant Q (Table D-15)

This plant treats 1,900 tons/day (1,724 metric tons/day) of zinc ore containing 2.5 percent zinc and 2.3 percent iron. It produces 75 tons/day (68 metric tons/day) of zinc concentrates at a grade of about 59 percent zinc and at a recovery of about 92 percent.

Cyanide is not used at present but has been used. Cyanide addition, when it was made to the zinc cleaner circuit, was only about 0.02 lb/ton (0.091 kg/metric ton) of feed.

The company operates under an NPDES permit which does not place limitations on cyanide. It is possible that cyanide may be used in the future, but the company is intending to close the mill circuit and eliminate mill discharge.

Staff members have experimented in the laboratory in the past with sodium sulfite as a depressant for pyrite and have found that it has not improved grade or recovery over those obtainable with no depressants.

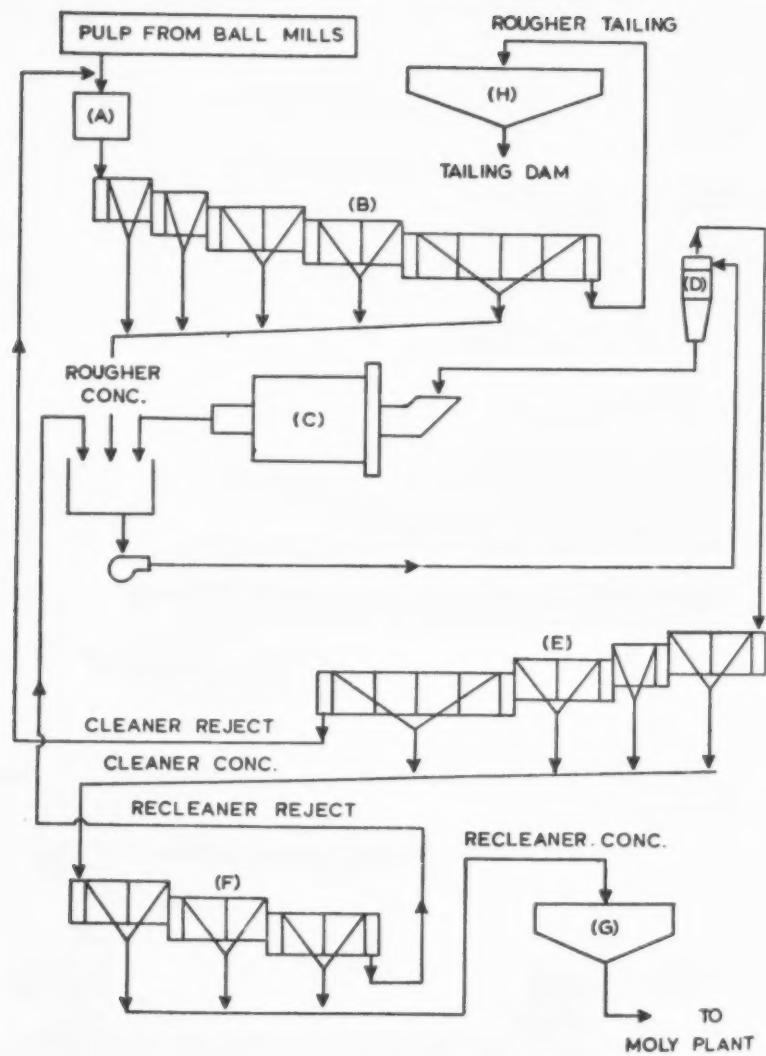
The company spokesman estimated that it would take about 2 days of mill operation to assess the value of reagent changes in the mill, but that a longer time would be needed to fine-tune the circuit.

APPENDIX E

FLWSHEETS OF TYPICAL MILLING OPERATIONS

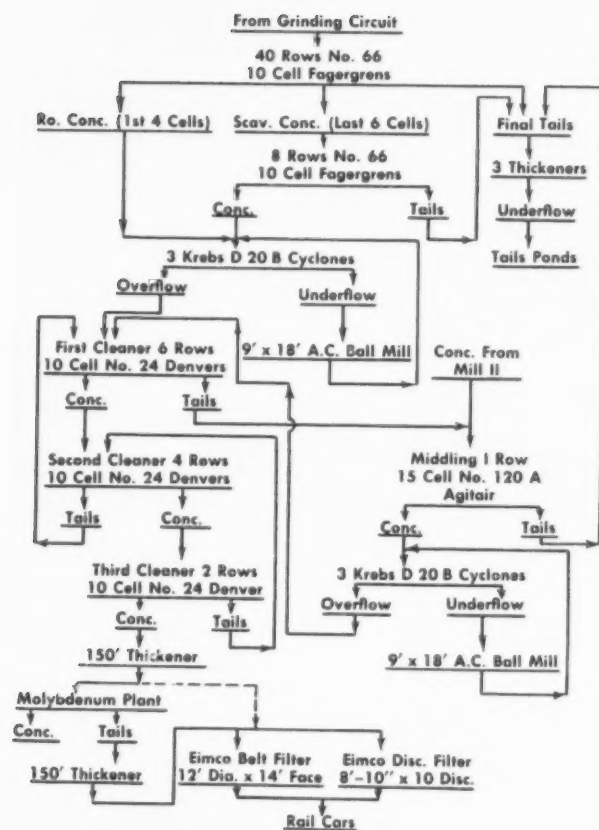
7

E-1



PRIMARY FLOTATION CIRCUIT FLOWSHEET

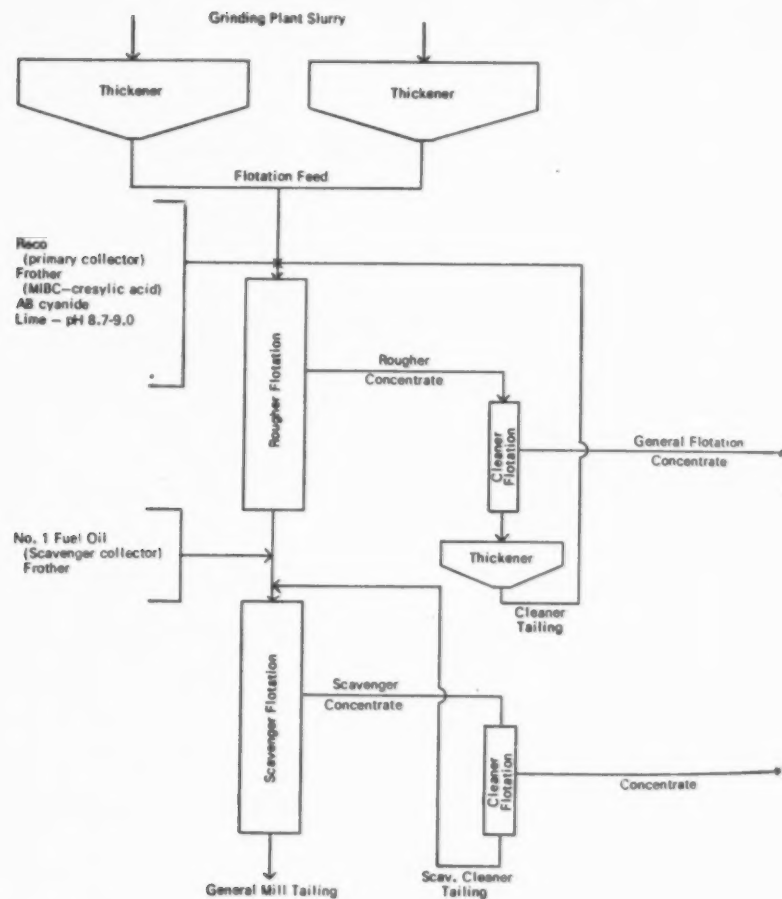
FIGURE E-1. PLANT B - ARIZONA (COPPER)¹



Mill I Flotation Flowsheet

FIGURE E-2. PLANT C - ARIZONA (COPPER)²

KENNECOTT COPPER CORPORATION - UTAH COPPER DIVISION



COPPER FLOTATION CIRCUIT FLOWSHEET

FIGURE E-3. PLANT G - UTAH (COPPER)³



E-4

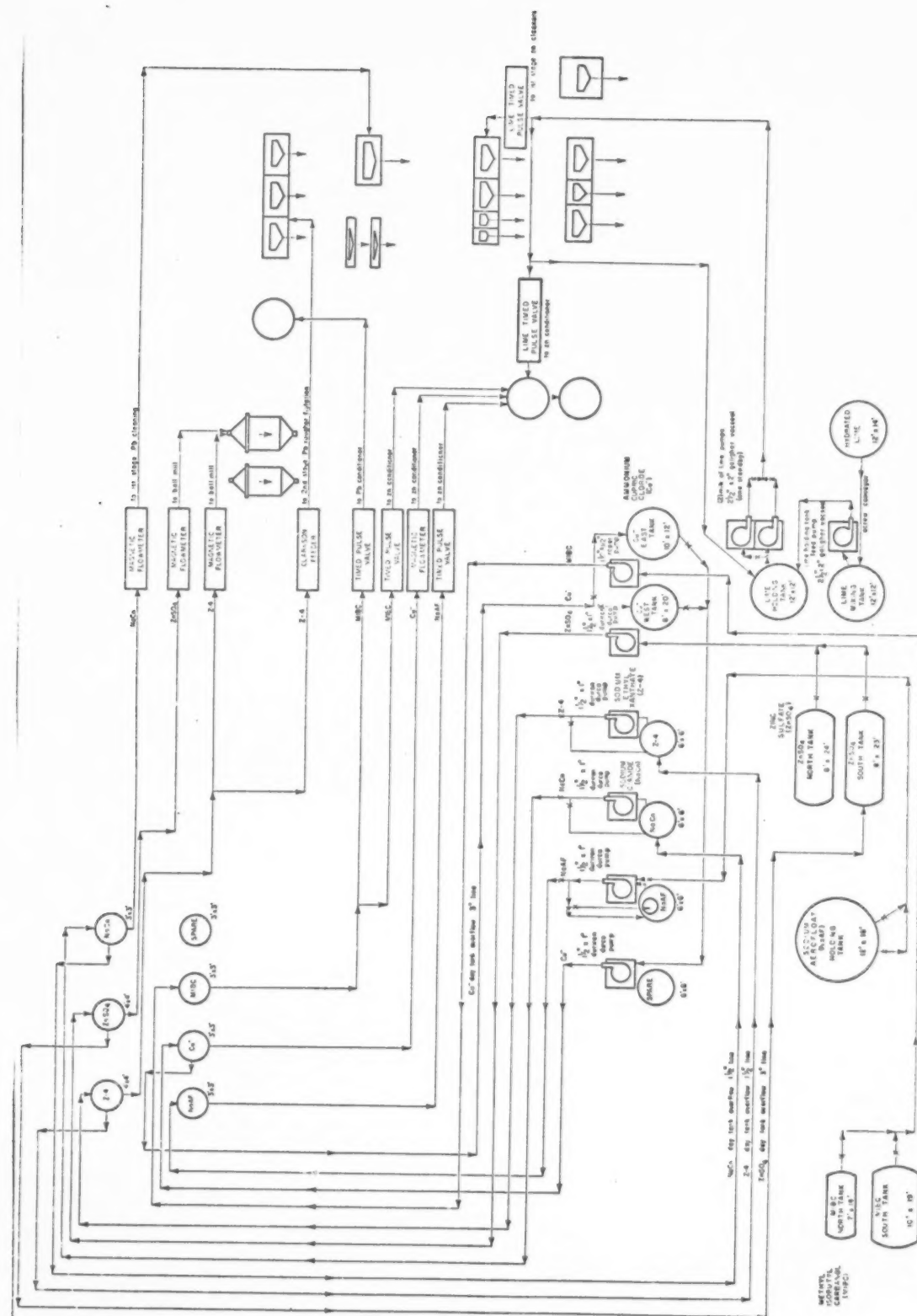


FIGURE E-5. PLANT M - MISSOURI (LEAD-ZINC)⁵

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1. Flotation, A. M. Gaudin Memorial Volume, M. C. Fuerstenau, Editor, Volume 2, American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc., New York, 1976, p. 1116.
2. Ibid., pp 1096-1097.
3. Ibid., p. 1070.
4. Ibid., p. 1219.
5. Furnished by interviewee.